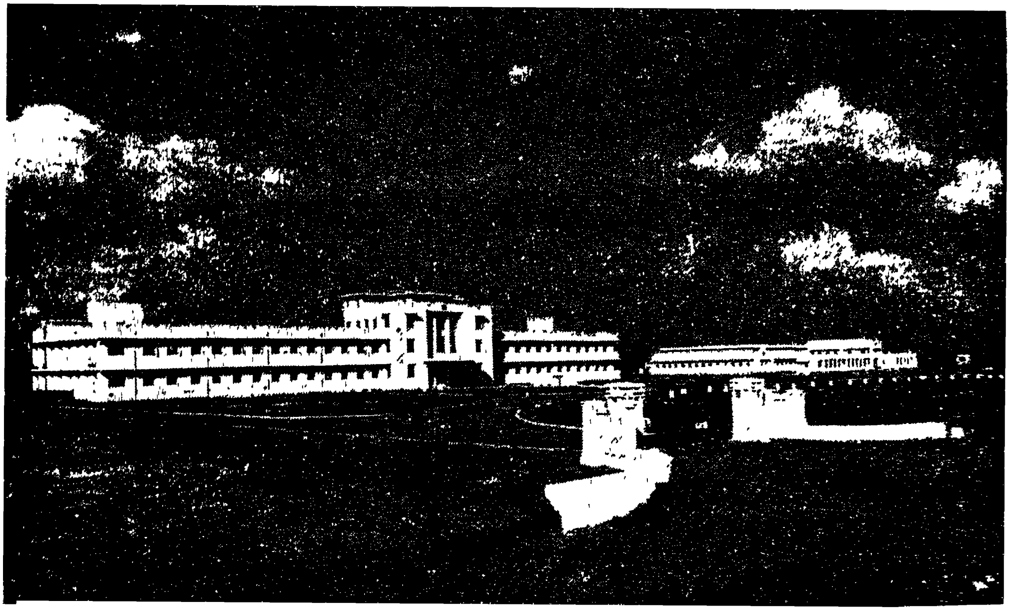
SYMPOSIUM

ON

LEATHER AUXILIARIES

(14*th*, 15*th*, 16*th* and 17*th* *March* 1958)

PROCEEDINGS AND PAPERS



Central Leather Research Institute,
ADYAR, MADRAS 20.
COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH-INDIA.
1959

Price Re. 1/-

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INAUGURATION OF THE LEATHER AUXILIARIES SYMPOSIUM AND THE LEATHER FAIR

The Symposium on Leather Auxiliaries and the Leather Fair were inaugurated on 14-3-1958 at the Central Leather Research Institute, Adyar, by the Union Finance Minister, Shri Morarji Desai and Prof. M. S. Thacker, Director-General of Scientific and Industrial Research, respectively.

The function was presided over by the Governor, Mr. Bishnuram Medhi. Over 180 delegates from all over India attended, besides delegates from the U.S.S.R. and the Philippines, distinguished guests, traders, technologists, tanners, manufacturers and officials.

Welcoming the gathering, Dr. Y. Nayudamma, Director of the Institute said that the Leather Industry was a major industry in Madras, fetching large amount of revenue and giving employment to a large number of people. It was in the fitness of things that His Excellency the Governor of Madras presided on this occasion. The popular Union Minister for Commerce and Industries and Finance Minister-Designate, who was in their midst, had affection not only for the Institute but also for the Leather Industry.

This Symposium was intended for bringing in various interests, for pooling of thoughts and sharing of ideas to arrive at some clear cut and well chalked out programme.

Mr. M. J. Jamal Mohideen, representing the Indian leather trade and industry, said India produced in a year about 20 million cattle hides—about 90% of them from animals dying of old age and natural causes—35 million goat skins and 17 million sheep skins, valued at about 400 millions of rupees in raw state. Of this about 17 millions of goat skins worth about 60 million rupees were exported in raw state itself. The rest was converted into leathers and leather articles valued at more than 500 million rupees. However, of these, 250 to 300 million rupees worth of leather and leather articles only were exported to foreign countries and the balance consumed internally. If wattle bark and mimosa extracts only were used for tanning all these, the industry would require about 67,000 tons of wattle bark and half that quantity of mimosa extract per annum. But the very fact that they were importing only about 7,000 tons mimosa extract definitely showed that the industry was using indigenous tanning materials to a large extent and was importing only the bare necessity. This import could be progressively reduced when wattle bark or some other tanning material equal in quality was available in large quantity to the industry in the country. He was glad that the Central Leather Research Institute had been from its very inception trying hard to tackle this problem, and had found some substitutes. He thought the institute had discharged its responsibilities in quite an appreciable manner.

Inaugurating the Symposium on Leather Auxiliaries, Prof. M. S. Thacker, pointed out how invaluable had been the help and advice given by Mr. Morarji Desai on problems facing the research laboratories. He would say that but for the help received from the Minister many of the researches made in the laboratories would not have been translated into industrial production.

Prof. Thacker observed that the work of research laboratories in the country—they had about 18 and the 19th one was in the course of establishment—were geared up to undertake and process the problems not only of what scientists thought it would be good for the country but of such problems which the industry would throw on to the laboratories.

He said that in order to make available to the industry outside, the results of the experiments undertaken by the laboratories, they were contemplating a proposal to establish extension services not only here but in other regions also. He would at the same time tell the industry 'Please let us have your problems and we shall tackle them.'

Prof. Thacker said he understood that whereas small industries were anxious to take what the laboratories offered them, the larger industries were not so inclined. He would make a request to the industrialists, large and small, that the laboratory was a joint venture and unless they and the Government worked together, 'We cannot go far ahead.'

Referring to the indigenous production of the auxiliary materials for the leather industry, Prof. Thacker said that scientific and technological contributions had been made by his colleagues in other parts of the world. They in the Council of Scientific and Industrial Research would await the deliberations at the Symposium with great interest and great expectations. He would also request the Association of Hides and Skins to pool their knowledge and experience of the work they had done towards auxiliaries with the work that had been done by the laboratory.

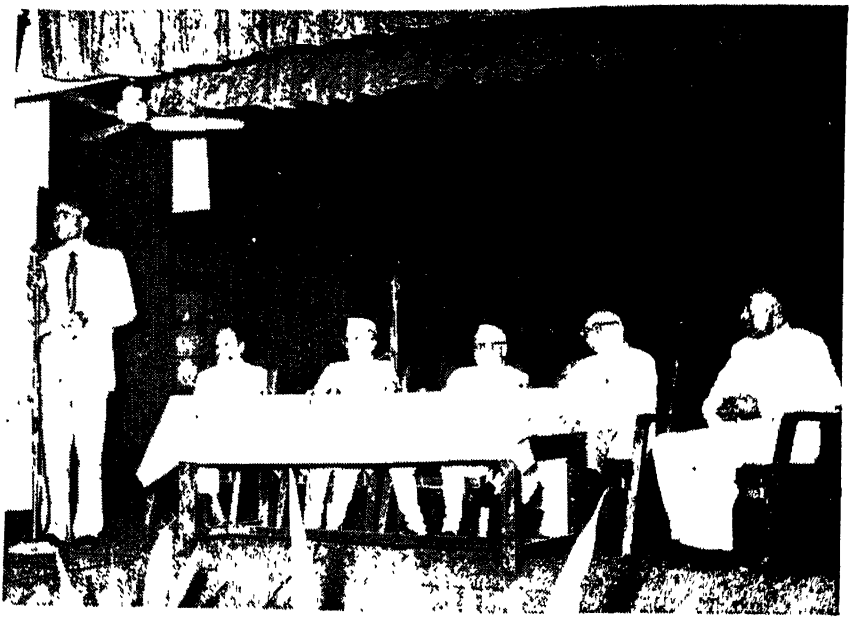
To his colleagues—the scientific workers in the laboratory—he would make a mention—the memorable mention of the announcement by the Prime Minister of the Scientists' Charter. He would not go into it.

Mr. Morarji Desai, inaugurating the Leather Fair, said that he had an opportunity some months back of going round the Institute and knowing what it had been doing. This was one of those great laboratories which had been started and which had been working very usefully. He was struck by the admirable work that had been done so far in the Institute, and was very happy to see that the leather industry of our country was considerably helped by the original and useful work that was being done there.

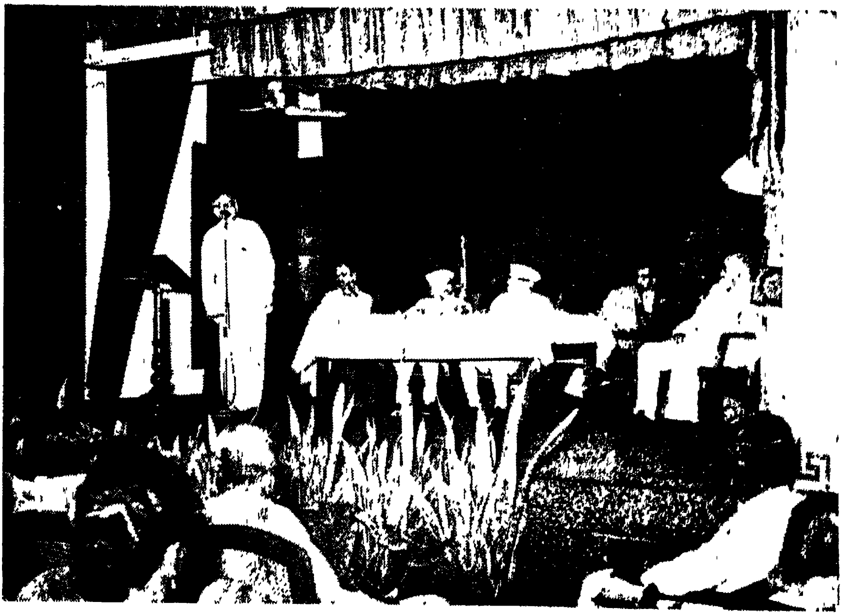
Mr. Morarji Desai said he was glad that the Leather Fair was organised because it was necessary for people to know where their leather industry stood, its possibilities, its actualities, advances so far made and yet to be made, so that full use could be made of the valuable work that was being done at the Institute, as elsewhere in the country. Researches were not made only as a result of good means or good buildings or good opportunities, but due to the intensity of purpose of those who were engaged in research work and more especially of the person who was in charge of the work and responsible for it. 'I do not think this Institute could have had a better Director than the one it has at present.' (Applause).

He said their attention should be directed to producing all that they wanted and even more than what they wanted so that they would be able to send out more and more things. He could not say they had reached the standards in tanning and finishing reached in some countries of the world which were very much advanced in this respect. They had yet to reach those standards and he had every hope that the work that was being done at the Institute would enable them to produce goods not inferior in either quality or usefulness but superior to any from elsewhere, because they had all the resources here to make the best leather. He hoped that the Leather Fair which he was inaugurating would be a step forward in this direction of making their leather industry the best in the world not from the point of view of

Prof. M. S. Thacker, Director-General, Scientific & Industrial Research, leading Shri Morarji Desai, (right), Union Minister for Industries and Commerce to the Inauguration Function.



Dr. Y. Nayudamma, welcoming the delegates and the distinguished guests at the Inauguration Function.



Prof. M. S. Thacker, speaking at the Inauguration Function.

competing with other people but from the point of view of utilising their resources—both human intellect and industrial resources—to the maximum capacity for the happiness of their own and other people.

The Minister added that leather was useful in every way. But it sometimes led them into the realms of cruelty. He only hoped that in their desire to have better and better leather they would not resort to methods which would involve cruelty to animals.

Prof. A. N. Mikhailov, a delegate from the U.S.S.R., conveyed on behalf of leather chemists and engineers of Soviet Russia their best wishes to the leather industry in India, and hoped the Institute would be of great benefit to the industry.

Messages of good wishes were received among others from the Speaker of the Lok Sabha, Mr. M. Ananthasayanam Iyengar, Union Ministers Mr. A. P. Jain and Mr. K. C. Reddi, the Speaker of the Madras Assembly, Dr. U. Krishna Rao and Foreign Leather Scientists.

Governor's Address

Mr. Bishnuram Medhi, who presided said the Symposium would give ample opportunities to the specialists to read and discuss technical papers on the various aspects of the industry. Problems of finding raw materials, supply of aids and auxiliaries in the various stages of production and manufacture and finding suitable markets could be discussed freely and frankly in order to formulate clear and constructive suggestions for the all-round improvement of the leather industry, he said.

The Governor added that from time immemorial, leather had always been used by human beings to cover their bodies. It was said that the use of leather was even more ancient than the use of barks. As human civilisation advanced and as man developed his wants and tastes, new processes were discovered in order to cure and preserve raw hides and skins and to give them better finish, and later to manufacture useful articles of ware with beautiful and delicate workmanship.

The Governor added that the South Indian tanning industry tanned hides and skins by vegetable tanning. Processes had been evolved by local tanners by practical experience over more than one hundred years. The utility and excellence of the products manufactured had been such as to find a market for them almost throughout the world. He further pointed out that Madras had also some of the biggest organised tanneries, producing a variety of finished leathers, industrial leathers and other leathers. The State had the unique privilege of having the first institution of leather technologists in India, *viz.*, the Institute of Leather Technology at Washermanpet, where foreman and certificate holders were trained both in the manufacture of leather and leather goods. Madras was also singularly fortunate in having one of the national laboratories, *viz.*, the Central Leather Research Institute.

Referring to the Five-Year Plans formulated with a view to improving their economy and bringing about all-round balanced development, the Governor said that they as specialists would have to take many aspects of the industry into consideration, exchange notes with others and formulate proposals for future expansion and improvement. He wished them all success in their deliberations.

Mr. M. A. Ghani proposed a vote of thanks.

The Leather Fair

Leather Fair was organised by a committee specially constituted for the purpose. The Fair was kept open from 14th to 29th March, 1958. Prof. Thacker, Shri Morarji Desai and the distinguished delegates and invitees went round the Fair after its inauguration.

The Fair was got up with the enthusiastic co-operation of no less than fifty participants representing the Leather and the Leather Auxiliaries Industry—E. I. Tanners, Manufacturers and Suppliers of Tanning Materials, Industrial Leather Manufacturers, organised industries producing a variety of leathers, Chrome tanners, Reptile Leather manufacturers, Suppliers and Manufacturers of various Leather Auxiliaries and Machinery and Leather Goods Industry. Exhibits were received from Germany, United Kingdom, United States of America, Burma, Indonesia and Japan also. The Fair elicited much interest and appreciation.

' At Home ' and dinner to the delegates

A committee of Hosts, representing the Leather and the Leather Auxiliaries Industries were ' At Home ' to the delegates to the Symposium, on 15-3-58 at the Central Leather Research Institute, Madras. Mr. M. Bhaktavatsalam, Home Minister, Madras State was the chief guest.

In welcoming the chief guest, Mr. C. K. Duraivelan said that the leather industry was bringing to the country about Rs. 24 crores worth of foreign exchange, sterling and dollar. He said that a problem facing the industry, was with regard to getting a good supply of raw hides, especially after the separation of Pakistan.

Mr. T. Abdul Wahid said that the E. I. Tanning industry had to be gradually replaced by the finished leather industry. He said that to-day the export of E.I. tanned leather had come down to 2,000 bales from 3,000 to 4,000 bales, which was due to the higher cost of production and the fact that foreign buyers were not prepared to pay high prices.

Mr. E. S. Subramanian next spoke. Mr. K. J. Kothari of Kharaghpur thanked the organisers of the Symposium for bringing together the technologists, the tanners and leather auxiliary manufacturers on a common platform.

Minister's appeal to tanners : Mr. Bhaktavatsalam, speaking next, said that the leather industry was very important to India in many ways, especially as an earner of foreign exchange. The Symposium was unique and very useful. He said that the Research Institute had been a most valuable acquisition of Madras State, and he hoped that the activities of this Institute would be expanded further before long. He also expressed the wish that more and more finished goods would be manufactured and exported to other countries fetching even more foreign exchange. He appealed to the tanners to take the fullest advantage of the results of researches conducted at the Institute by enthusiastic, able and devoted research workers. He assured that the Government would extend their help in solving the problems and difficulties which faced the industry. The E. I. tanned leather had won a great reputation in foreign countries and he appealed to the tanners to keep up the reputation.

Mr. N. Viswanathan of Calcutta proposed a vote of thanks.

After the function, there was a programme of entertainment.

Shri Bishnuram Medhi, Governor of Madras State, delivering his Presidential Address at the Inauguration Function.

Shri Morarji Desai, Shri Bishnuram Medhi, and Prof M. S. Thacker at the C. L. R. I. Stall in the Leather Fair.

Raja Sir Muthiah Chettiar, Member, Executive Council, Central Leather Research Institute, speaking, at the Dinner to the delegates. To his right are, in order (1) Dr. A. L. Mudaliar, Chairman, Executive Council, C. L. R. I. (2) Mr. R. Atkins (of the Carborundum Universal Ltd), President of the Committee of Hosts, (3) Prof. M. S. Thacker and (4) Dr. Y. Nayudamma.

Prof. A. N. Mikhailov, delegate from the U.S.S.R. speaking at the Dinner. Mr. Goldobenkov, the other U.S.S.R. delegate is to his left.

The delegates were entertained to a Dinner on 16-3-58 by the Committee of Hosts, at the Central Leather Research Institute with Dr. A. Lakshmanaswamy Mudaliar, Chairman, Executive Council of the Central Leather Research Institute and Vice-Chancellor, University of Madras, as the chief guest.

Mr. R. Atkins of the Carborundum Universal Ltd., President of the Committee of Hosts, welcomed the gathering. Shri A. Nagappa Chettiar of the India Leather Corporation and Shri T. V. Jagadeesan of the Standard Vacuum Oil Company spoke on behalf of the hosts. Shri Chettiar announced on this occasion that his donation of Rs. 2,500 for instituting a scholarship at the Central Leather Research Institute would be tenable for one year. Shri M. A. Muthiah Chettiar, Rajah of Chettinad and Prof. M. S. Thacker, also addressed the assembled guests and Prof. A. N. Mikhailov of the U.S.S.R. replied on behalf of the delegates. The chief guest, in the course of his speech referred in appreciative terms to the work of the Institute. Shri U. A. Menon of Messrs. Gordon Woodroffe Leather Manufacturing Co. Ltd., proposed a vote of thanks.

Earlier, the delegates witnessed a Bharata Natyam dance performance by Kumaris G. Vasanti and G. Srimani.

On the last day of the Symposium, there were special lectures by the Russian Delegates about Leather Research and Leather Industry in the U.S.S.R.

PROCEEDINGS OF THE TECHNICAL SESSION I

15th March, 1958, Forenoon

Chairman : Dr. A. Seetharamiah, Development Wing (Leather), Ministry of Commerce and Industry, Government of India.

Recorder : Dr. S. M. Bose, Central Leather Research Institute.

Dr. S. K. Barat introduced the Chairman.

After initiation of the Session by the Chairman, papers were read as follows :

Studies on Khari Salt, Part I ...	Read by Mr. S. C. Nandy, C.L.R.I.
Assessment of the utility of certain commercial samples of lime.	Read by Mr. T. S. Krishnan, C.L.R.I.
Possibility of use of barium sulphide as a substitute for sodium sulphide in tanning industry.	Read by Dr. V. S. Padmanabhan, C.L.R.I.
Enzyme bates and depilants for leather manufacture.	Presented by Dr. S. M. Bose, C.L.R.I.
Some techniques for enzyme bate production and their uses.	Read by Mr. S. C. Dhar, C.L.R.I.
Application of versene for determination of Ca and Mg in salts used for curing hides and skins.	Read by Miss A. Nagasiromani, C.L.R.I.
Instrumental methods for assessment of leather auxiliaries.	Read by Dr. D. Ramaswamy, C.L.R.I.
Influence of different tanning auxiliaries on the swelling of hide protein.	Read by Dr. S. Ghosh, C.L.R.I.
Leather Auxiliaries and their uses in the manufacture of leather.	Read by Dr. V. S. Padmanabhan, C.L.R.I.
Problems facing Leather Auxiliary Industry in India.	Taken as read.
Leather and other allied industries in new Mysore State.	Read by Dr. V. S. Padmanabhan C.L.R.I.
Auxiliaries for leather manufacture.	Read by Mr. N. Viswanathan, Chemicolour Ltd.
A few indigenous chemicals for tanning in leather industry.	Summary presented by Dr. V. S. Padmanabhan, C.L.R.I.

STUDIES ON KHARI SALT—PART I

S. C. NANDY AND S. N. SEN
(*Central Leather Research Institute, Madras*)

ABSTRACT

Khari salt is one of the important curing agents available in India, especially for dry salting hides and skins. Khari salt is known to be composed of different constituents with a considerable amount of earthy matters. The suitability of Khari salt as a curing agent for dry salting has been studied in relation to its moisture absorption in different humid conditions.

Dry salting is one of the most common methods of curing and preserving hides and skins and has been largely adopted in Indian trade, especially for curing skins. In a country like India having varieties of climatic conditions it is very difficult to preserve dry salted hides and skins for a considerable period in some parts of the country and in particular seasons. This is because sodium chloride is hygroscopic in humid atmosphere and the more so if calcium and magnesium chlorides are present as impurities. Das, Dhavale, and Pal have therefore recommended a mixture of salts (5 parts of anhydrous sodium sulphate to 1 part of sodium chloride) to be used in dry salting instead of common salt alone.

Khari salt, another type of salt available in India, is especially suited for dry salting purpose. This salt appears as an efflorescence on the soil in some parts of North Bihar. Khari salt has got the distinct advantage that, it does not absorb moisture from the air as is the case with common salt, and as such the stock cured with it is preserved better in humid conditions than the stock cured with common salt. Khari salt is generally used in West Bengal, Bihar, some parts of Uttar Pradesh and to a little extent in Madras. This salt is actually a mixture of different ingredients and its chemical composition is highly variable. The most common constituents are sodium sulphate, magnesium sulphate and sodium chloride (with good proportion of insoluble earthy matter)[2]. The proportion of the above constituents in the water soluble fraction has been reported to be as follows :

Na_2SO_4%	$MgSO_4$%	NaCl%	Ref.
69.3	21.4	4.62	(2)
70.0	16.1	1.3	(2)
60.0	24.3	11.3	(2)
46.66	53.33	...	(3)

Thus it can be seen that Khari salt is mainly composed of sodium sulphate and magnesium sulphate. Although it is considered as an efficient curing agent, little work has been done on different aspects of its suitability. It has also got some drawbacks, *e.g.*, little or no bacteriostatic action, high percentage of insoluble matters, muddy appearance etc. Considering these factors a thorough study on the curing property of Khari salt both for dry salting and wet salting has been undertaken. In the present work, this salt has been studied in relation to its mode of moisture absorption in humid conditions.

Experimental

About 5 gm. of finely powdered crude Khari salt or other salts were weighed accurately in petri dishes and then kept at particular humidity and temperature under control. At different intervals of time the petri dishes were taken out and weighed. The humidity was controlled in big desiccators with different concentrations of sulphuric acid. The percentage of moisture absorption has been expressed in each case and results obtained in different experiments are represented graphically in Figures 1 to 4.

Discussion

Effect of humidity on moisture absorption by Khari salt : The moisture absorption of Khari salt was tested for a period of 15 days at the following relative humidities, 60%, 70%, 80%, 90% and 100% maintained at a temperature of 28°C. ± 1°. The results of Fig. 1 clearly show that the higher the relative humidity, the greater the absorption of moisture by Khari salt. At lower relative humidities, *e.g.*, 60% and 70%, the amount of moisture absorbed is very little and also the progressive rate of increase within this observation period of 15 days, is practically negligible. The rate of increase in moisture absorption is quite appreciable at higher humidities and increases as the humidity reaches saturation. The results indicate that hides and skins cured with Khari salt will probably absorb moisture when subjected to highly humid conditions during storage.

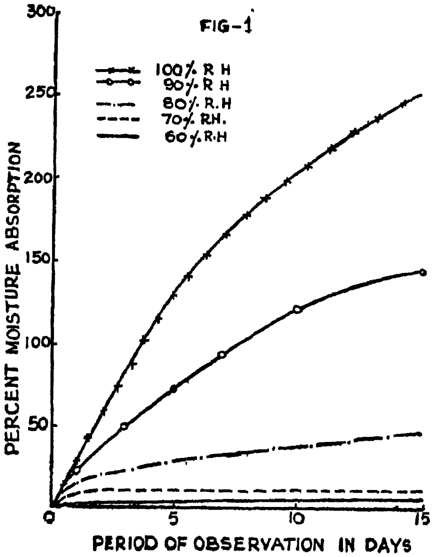


FIG-1

Effect of grain size of Khari salt on moisture absorption : Khari salt is generally obtained in the form of big or small lumps. It has been observed that the salt in lumps does not absorb so much moisture even in a high humid condition. But in curing, Khari salt is applied in the form of powder or in solution. So the extent of moisture absorption of Khari salt in the form of lumps was compared with that of powder form. In this experiment the humidity was kept at 90% and the temperature at 28°C. ±1°. The period of observation was 10 days. It is evident from Fig. 2 that the rate of moisture absorption in the case of powder is considerably greater than that of the lump, practically double. Most probably such a wide variation is due to the large exposed area of the surface in the case of the powder.

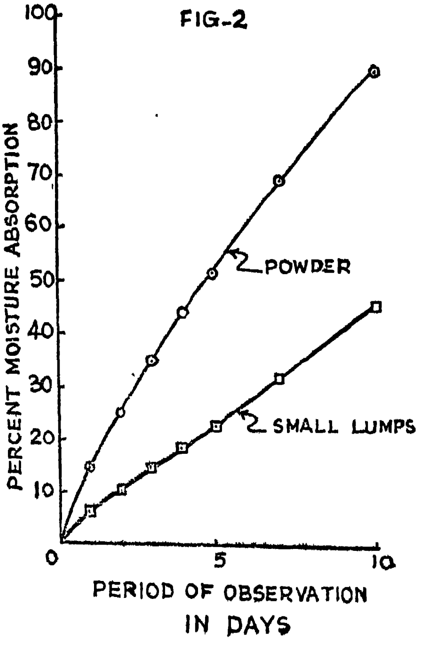


FIG-2

Effect of temperature on the moisture absorption of Khari salt : It was assumed that there might be some correlation between the moisture absorption by Khari salt and the prevailing temperature. In this experiment the moisture absorption of Khari salt at 100% R.H. was determined at temperatures of 18°, 28° and 45°C. and the period of observation lasted for 7 days. It will be observed from Fig. 3 that, the moisture absorption increases with the rise of temperature, and the increase in the moisture absorption is much less upto 28°C. but is appreciable at 45°C. Thus it is obvious that preserving a dry Khari salted hide or skin at a lower temperature will be of definite advantage.

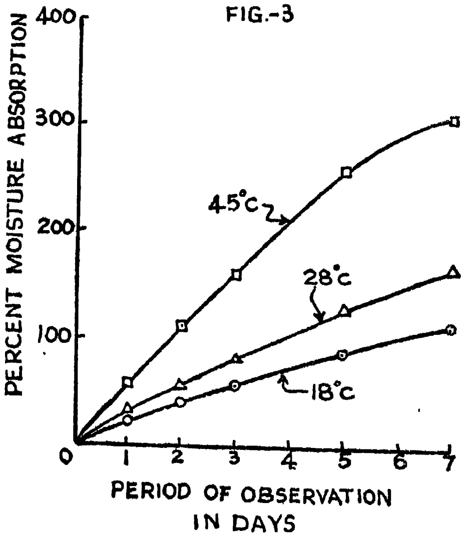


FIG.-3

Nature of moisture absorption of different salts : It has been already pointed out that Khari salt is a mixture of different components, sodium sulphate, magnesium sulphate and sodium chloride being the principal constituents. So, it may be of interest to find out the nature of moisture absorption by these components in pure form and to compare these with that of Khari salt. It was also decided to verify the moisture absorption of Khari salt free from insoluble impurities ('pure' Khari salt) with that of crude one. The water soluble fraction of crude Khari salt was evaporated over a water bath and the 'pure' Khari salt obtained was powdered and used in the experiment. Analytically pure varieties of sodium chloride, sodium sulphate (anhydrous) and magnesium sulphate (hydrated) were used. The percentage moisture absorption was determined at 100% R.H. and a temperature of 28°C. over a period of 15 days.

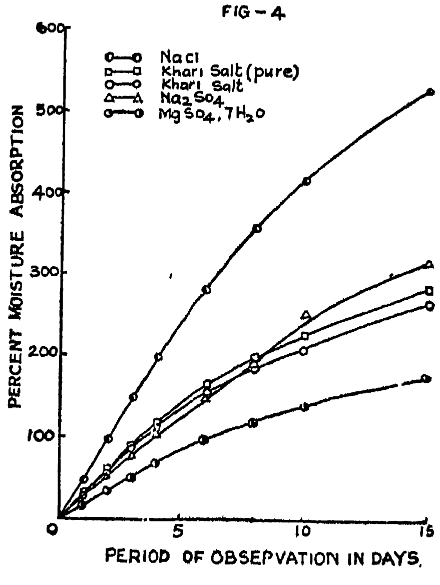


FIG-4

It is clear from Fig. 4 that the different compounds vary regarding their nature of moisture absorption. The moisture absorption is maximum in the case of sodium chloride and minimum in the case of magnesium sulphate. The curves representing the moisture absorption of two varieties of Khari salt and sodium sulphate proceed close to each other upto a period of about

8 days after which slight variation results. It can be observed that the percentage moisture absorption is more in case of 'pure' Khari salt than that of crude one. Innes[4] has pointed out that pure sodium chloride is highly hygroscopic in damp climatic conditions. The results of this experiment confirm his findings. It is also pointed out by Innes that anhydrous sodium sulphate can absorb moisture upto some limit, *i.e.*, until it is converted into the hydrated form ($Na_2SO_4 . 10H_2O$). It seems from the figure, that within this period of observation (15 days) the anhydrous sodium sulphate has not been completely converted into the hydrated one. One interesting feature of the figure is that the rate of moisture absorption of Khari salt, either crude or pure, nearly approaches that of sodium sulphate. Such a proximity may be explained in relation to the chemical composition of Khari salt. It is known that about 60–70% of Khari salt is sodium sulphate. Out of the other two components magnesium sulphate shows less and sodium chloride more moisture absorption than sodium sulphate. But it can be easily assumed that the moisture absorption of a mixture of magnesium sulphate and sodium chloride in the proportion mentioned earlier will be the resultant absorption of two individual compounds, and will also nearly approach that of sodium sulphate. The above results therefore indicate that dry salting with Khari salt or sodium sulphate or magnesium sulphate will be definitely advantageous in case the cured stock is to be preserved in a damp condition.

But it should be borne in mind that the rate and extent of moisture absorption in case of cured hide or skin will not be so rapid and progressive due to different physicochemical conditions. However, experiments with actual cured hide or skin will be carried out in near future and the results will be reported later on.

Summary

(1) Khari salt is hygroscopic in a highly humid atmosphere. The rate of moisture absorption is negligible upto 75% R.H., then slowly rises upto 80% and then it becomes prominent at 90% and 100%.

(2) It has been observed that Khari salt when in finely powdered form absorbs more moisture than in the form of lumps.

(3) The rate of moisture absorption of Khari salt is largely influenced by temperature. The moisture absorption increases with the rise of temperature at least within the limit so far observed.

(4) At 100% R.H. the hygroscopic property of pure sodium chloride is found to be the highest and that of magnesium sulphate the lowest. The hygroscopic property of Khari salt both 'pure' and crude and that of sodium sulphate (anhydrous) approach each other and lie in between that of sodium chloride and magnesium sulphate.

ACKNOWLEDGEMENT

Thanks are due to the Director, Central Leather Research Institute, for permission to present the paper in this symposium.

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ASSESSMENT OF THE UTILITY OF CERTAIN COMMERCIAL SAMPLES OF LIME

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ABSTRACT

Some samples of lime and calcium carbide have been tested in regard to their use in the leather industry.

The age old saying that " good leather is made in lime yard " is definitely no exaggeration. It may be worthwhile here to briefly bring out the different functions of liming and the effects that it produces on the hide. In liming, the hair is loosened, the fats are saponified and the hide gets plumped up which makes it easier to remove the unwanted adipose tissue. A proper amount of splitting up of collagen fibres is necessary to obtain the desired quality of leather, this splitting up being effected in the course of liming. From the foregoing, it may be seen that this operation should be controlled such that the required effects are got.

Large quantity of lime is being consumed in the leather industry. Especially in the traditional process of E.I. tannage, lime is invariably employed without any sharpening agents like Na_2S etc. The chief sources of lime are (1) Lime stone, (2) Shell lime. The commercial samples of lime contain in addition to CaO, calcium carbonate with other minor constituents like $MgCO_3$ silicates, ferric oxide, alumina etc. $CaCO_3$ content varies depending upon the location and when different methods of calcination are resorted to, variations in the resulting quick lime content (CaO content) are accentuated. Therefore it was felt desirable that studies be undertaken to compare the liming effects of limes from different sources.

Experimental

Six different commercial samples of lime were taken and the available CaO was determined in each case. (Table 1).

Table 1

	Available CaO (Percent)
A—Mettur slaked lime	64.21
B—C.L.R.I. Shell Lime (Slaked) ...	39.96
C—Carbide dust	51.3
D—Mettur burnt lime Grade I ...	86.58
E—Mettur burnt lime Grade II	81.94
F—Mettur burnt lime Grade III ...	38.56

Liming trials were done as follows :

The butt portion of a w/s buffalo hide was soaked for 3 hours, washed thoroughly in different changes of water. The well soaked and well washed material was cut into 6 pieces and the pieces were weighed after draining them for 1 hour. The pieces were limed with different samples of limes. Lime corresponding to 10% available CaO on soaked weight was used in each case the water used being 400%. The pieces remained in lime for 8 days with daily handling. On the 9th day the pieces were unhaired, allowed to drain for 1 hour and the weights determined. They were again relimed with 50% available CaO and 400% water for 4 days with daily handling. On the 13th day, the pieces were fleshed, drained for 1 hour and the fleshed weights determined. (Table 2).

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Table 2

Sample	Kind and source of lime	Soaked weight in gms.	Weight after unhairing in gm	Per cent gain in weight over soaked weight	Fleshed weight in gms	Per cent gain in weight over soaked weight
A.	Mettur slaked lime ...	312	554	177.5	433	138.8
B.	C.L.R.I. slaked shell lime	321	527	164.1	408	127.2
C.	Carbide dust	361	662	182.8	514	142.
D.	Mettur burnt lime Grade I	321	534	166.0	451	140.5
E.	Mettur burnt lime, Grade II	333	565	169.6	485	145.6
F.	Mettur burnt lime, Grade III	379	618	163	511	134.8

The depilation was good in the case of C (Carbide dust) whereas there were some short hairs in B and F (C.L.R.I. shell lime and Mettur burnt lime III) and larger amount in A, D and E.

After unhairing the percentage gain in weight over soaked weight was in the following order: C > A > E > D > B > F.

After fleshing, the percentage gain in weight over soaked weight was in the following order : E > C > D > A > F > B.

Carbide dust was found to be the best, with regard to unhairing and plumping.

These differences have arisen even though the same amount of CaO was used in all cases. Probably, they may be due to the different sources of lime. Thus it may be seen that besides the chemical composition namely the available CaO, the physical properties like density, porosity, particle size etc., also are of importance. Lime has a limited solubility in water which is no doubt an advantage in that the controlling of the operation is rendered easier. Because of this property, we encounter the difficulty of not getting enough lime in solution if lime is of poor quality. The milk of lime should be in the form of good stable emulsion and the undissolved $Ca(OH)_2$ should also be solubilised as rapidly as possible since otherwise the concentration of $Ca(OH)_2$, which is being continuously used up by hide for the liming effects, is reduced. Such dissolving of lime particles depends upon their size and density. Moreover the lime soaps that are formed should be much softer in consistency.

Different types of limes from different sources may cause lime soaps differing in consistency. The softer the soap, the greater will be the penetration of tanning and a uniform tannage with good grain is obtained. Such softer soaps are likely to be formed if quick slaking limes are used. In defective limes, the particles are bigger in size, less porous and more dense. These drawbacks arise, among other causes from the variation in source, composition and structure of lime stone and the method of calcination.

Improper handling and exposure of quick lime during cooling and storage periods contribute to the poor quality of lime. Quick lime has great affinity for CO_2 and water. The percentage of uncombined CaO is decreased, by the chemical combination of quick lime with CO_2 and water that are present in atmosphere. The pores of quick lime may get blocked by $CaCO_3$.

Thus a lime showing an excellent chemical analysis may be giving poor efficiency.

It is clearly evident that a proper method of calcination of lime stone or shell-lime of good composition and structure, is, in addition to the extreme care one has to take in slaking the lime and storing it carefully, of paramount importance in obtaining high efficiency of liming. Supply of standard grade of lime to the tanning industry is, therefore, very necessary.

DISCUSSION

*Mr. S. Nagarajan**(*S.I.S.I.*) : The suitability of calcium carbide waste dust was referred to us by a firm. The dust has got to be converted into hydroxide and slaked.

THE POSSIBILITY OF THE USE OF BARIUM SULPHIDE AS A SUBSTITUTE FOR SODIUM SULPHIDE IN TANNING INDUSTRY

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ABSTRACT

Complete depletion of the natural deposits of sodium sulphate in Rajasthan has considerably affected the sodium sulphide industry and the price of the product has nearly doubled. The tanning industry, as a result, has also been adversely affected. The present paper deals with the possibility of the use of barium sulphide as a substitute in the tanning industry.

The object of this paper is to focus the attention of research workers in the leather field and the tanners on the possibility of the use of Barium Sulphide as a substitute for Sodium Sulphide in tanning industry.

Sodium sulphide has been widely used as a sharpening agent in tanning industry. The annual demand of this chemical in India is of the order of 4,000 tons, out of which the tanning industry claims about 25%, the balance is taken up by the textile, paper and the chemical industries. Prior to 1956, this demand was to a very large extent met by indigenous production. Since then, production has gone down considerably. This drop in production is not due to any technical difficulty, but to the shortage of raw material, sodium sulphate. The sodium sulphide industry draws its requirement of salt cake from various sources, namely the bye products of the rayon, bichromate and hydrochloric and nitric acid plants. But by far the biggest source was the natural deposits of sodium sulphate in Rajasthan. In fact, this deposit used to cater to more than 80% of the sulphide requirements of the paper mills, glass works, textile mills and the medical profession. Complete depletion of the natural deposits in Rajasthan has considerably affected all the consuming industries. The sulphide industry, in particular, has been very hard hit, so much so that about half a dozen plants have been forced to close down. The price of sulphide has meanwhile gradually shot up and at present it stands at Rs. 1,000 a ton, which means a rise of 65%. To meet the demand, import had to be liberalised ; and during the first half of 1957, about 1,300 tons of sulphide had to be imported at a cost of Rs. 10 lakhs. This being the background, industries consuming sodium sulphide have to look for a suitable substitute.

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There is very little reference in the existing literature about the use of barium sulphide in tanning industry, though its depilatory property is well-known. The factors which point to the possibility of its use in tanning industry may be summed up as follows :

1. The swelling value of hides in Na_2S and barium sulphide has been studied in equivalent solutions by I. Criscuolo and the figures given by the author are 229 and 205 respectively. This shows that the swelling property of barium sulphide is slightly less than that of sodium sulphide.

2. The unhairing property of barium sulphide has been described by the same author to be similar to that of calcium sulphide, but the action is much less strong.

3. Commercial sodium sulphide is known to contain iron in the form of sulphide to the extent of 1.5 to 2%, in addition to other impurities like sodium carbonate, sulphite, thiosulphate and polysulphides. With the exception of ferrous sulphide, none of the other impurities have any detrimental effect on leather in bark tanning. Ferrous sulphide impurity in sodium sulphide sometimes gives rise to stains in leather. This impurity seldom exceeds 0.1% in the case of barium sulphide. The possibility of getting stains in leather in this case is much less.

4. Last, but by far the most important point is the price. Barium sulphide is only half as costly as sodium sulphide, as the manufacture is only a single stage operation. The cost of production of BaS is round about Rs. 250 a ton. If other factors are comparable, then the price index alone should favour the use of barium sulphide.

Large deposits of barytes are available in the country in Andhra Pradesh, Bihar and Rajasthan. The manufacture of barium sulphide can easily be taken up by any existing sulphide plant in the country. All that is necessary is to create a potential demand for the material.

REFERENCE

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DISCUSSION

Mr. V. Pandit, (Western India Tanneries Ltd., Bombay) : I would like to know what the sources of barium sulphide are and the quantity available.

Dr. Y. Nayudamma (in the absence of the author) : I am assured by the author that there is plenty of barium sulphide that could be made available to the industry if it is found useful.

Dr. D. Ramaswamy (CLRI) : (i) What will be the economics of barium sulphide production, whether it is half the cost of production of sodium sulphide as claimed by the author. Many of the barium compounds so necessary for other industries could be then made from barium sulphide, (ii) whether barium sulphide would be available for unhairing, (iii) what about the solubility of barium sulphide as compared to that of calcium sulphide.

Dr. Y. Nayudamma: The author's contentions are as follows:—(i) Barium sulphide is simple to make and cheaper to supply, (ii) Calcium sulphide cannot be used like barium sulphide, which is more soluble, (iii) the question has been posed to the leather technologists to try it out for liming, unhairing, etc., and I have promised that we will try it in our tannery.

Mr. J. Krishnamurthy (B. & C. Mills) : Barium sulphide is available with us and the industry could explore its uses.

Dr. Y. Nayudamma : It is proposed to do this in the Central Leather Research Institute Tannery.

Mr. N. Viswanathan (Chemicolour Ltd.) : Can calcium sulphide be used for unhairing ?

Mr. Ramaswamy (Mettur Chemicals) : Calcium sulphide is sparingly soluble.

THE PREPARATION OF SODIUM HYDROSULPHIDE

BY

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(Central Leather Research Institute, Madras)

ABSTRACT

Sodium hydrosulphide is used extensively in foreign countries as a sharpening agent for depilating purpose as it possesses some advantages over sodium sulphide. Attempted preparations of the compound are discussed in the paper. The difficulties in preparation consequent upon the unstable nature of pure sodium hydrosulphide are outlined.

Sodium sulphhydrate NaSH is acclaimed to be a better sharpening agent for depilation of hides and skins than sodium sulphide possibly due to the non-formation of sodium hydroxide. Sodium sulphide, hydrolyses to a large extent in water giving rise to sodium sulphhydrate and sodium hydroxide as per equation $Na_2S + H_2O \rightarrow NaHS + NaOH$. The resulting NaOH may have undesirable effects on the grain and the cohesion of fibre structure during liming process.

It has become the avowed practice in foreign countries, especially in America[1], to use only sodium sulphhydrate and little of sulphide during the liming operation. Further the use of sodium sulphhydrate has been found to be economical, 60% of the material itself being sufficient. Leathers prepared by using sodium sulphhydrate have been found by Pal and Das[2] to possess smoother grain. Two products are available commercially, one from Hooker's as flakes and the other from I.C.I. as concentrated solution (about 40–50%).

Work was undertaken at the Central Leather Research Institute in a preliminary manner to explore the possibilities of preparing this sharpener from available raw materials.

A solution of sodium hydrosulphide is easily obtained by passing H_2S through a cooled solution of sodium hydroxide or sodium carbonate.

$$NaOH + H_2S \rightarrow NaHS + H_2O$$

$$NaHS + NaOH \rightleftarrows Na_2S + H_2O$$

$$Na_2CO_3 + H_2S \rightarrow NaHS + NaHCO_3$$

$$NaHCO_3 + H_2S \rightarrow NaHS + H_2CO_3$$

The slight acidity developed due to formation of H_2CO_3 is favourable for the stability of NaHS and hence the reaction proceeds to a greater degree with Na_2CO_3. In the presence of NaOH, there is always some contamination of sodium sulphide.

The main difficulty was encountered while trying to crystallise the NaHS, as its trihydrate. Sodium sulphhydrate is very unstable and its crystals are very deliquescent, decomposition starting from 40°C. itself.

$$2NaHS \rightarrow Na_2S + H_2S.$$

Hence the solution could not be concentrated on a water bath. However, under reduced pressure, at a temperature below the decomposition point and in an atmosphere of H_2S some improvement was achieved ; however pure NaHS crystals could not be obtained.

The analysis of sodium sulphhydrate is somewhat indirect. The nitroprusside test which gives violet colour with sulphide and indigo blue colour with sulphhydrate could not be applied to the solutions since even in the case of sulphide, SH ion was invariably present due to hydrolysis.

$$Na_2S + H_2O \rightarrow NaHS + NaOH.$$

The method as suggested by Treadwell and Hall[3] was employed for the estimation and analysis of mixtures. The method consists in adding to the solution standard iodine solution and standard acid for decomposing the sulphide and sulphhydrate and estimating excess iodine (with standard $Na_2S_2O_3$) and the remaining acidity. The reactions taking place are

$$Na_2S + 2HCl \rightarrow 2NaCl + H_2S$$

$$NaHS + HCl \rightarrow NaCl + H_2S$$

$$H_2S + I_2 \rightarrow 2HI + S.$$

Even if a concentrated solution of sodium sulphhydrate were to be prepared and marketed for the use of tanners by the method suggested above, the difficulty for a commercial preparation will still be to get hydrogen sulphide in large quantities in a suitable container.

Another attempted method of preparation consisted in trying to prepare calcium sulphhydrate. No data relating to the properties and the stability of this compound are available in the literature excepting that it is soluble in water and perhaps more stable than NaHS.

H_2S was passed through saturated milk of lime solution with agitation when a bluish grey paste was obtained. The crystallisation of the hexa-hydrate was found to be difficult due to decomposition to sulphide and H_2S. Another method consisted in passing hydrogen sulphide through a dispersion of calcium sulphide in water $CaS + H_2S \rightarrow Ca(HS)_2$. A third method consisted in treating a solution of calcium sulphide with $NaHSO_4$. In these methods, the difficulty was mainly due to the poor solubility of calcium sulphide.

The electrolytic method utilising either $NaHSO_3$ or Na_2S as raw material in a partitioned cell was also thought of but could not be accomplished due to various difficulties. However the field is promising.

Further work on increasing the stability of sodium sulphhydrate is in progress. If the problem is tackled economically and if the chemical is put in the market, it will be of great help to the tanners.

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ENZYME BATES AND DEPILANTS FOR LEATHER MANUFACTURE

BY

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ABSTRACT

Enzyme bates and depilants are important leather auxiliaries. A review of the researches carried out at the Bio-chemistry Laboratory of the Central Leather Research Institute on the production and uses of enzyme bates and depilants for leather manufacture is presented. The merits and demerits of unhairing by enzymes and the possibility of using enzymes as dewooling agents and as soaking agents are also discussed. Several aspects of the action of bating enzymes on skin constituents are also explained.

It is well known that enzyme bates are essential auxiliaries for modern leather manufacture ; the demand by the Indian Leather Industry for these is met solely by import. No reliable statistics, however, are available regarding the import or total consumption of enzyme bates in India. The consumption of the ' Pancreol ' bate as estimated by the Planning Commission, Government of India, is of the order of 60 tons annually. This figure seems to give a very low estimate of the consumption of bates in India. No accurate data on the consumption of other imported bates like ' Cutrilin ' and ' Pancolin ' are available.

If the consumption of enzyme bates is calculated on the basis of the amount of the upper leather produced in India, it may be seen that out of the total production of cow hides in India which is estimated at about 161 lakh pieces, about 15 per cent only, that is, 24 lakh pieces only are used for the chrome tanning as reported in the Report on the Marketing of Hides in India and hence this would require about 214 tons of bates, taking average pelt weight as 20 lbs. per piece and bating material used as 1 per cent on the pelt weight. Since glace kid is at present manufactured in three or four tanneries in India, the approximate quantity of the bating material required for the production of glace kid may be of the order of 20 tons per year. Although it may be possible to estimate the requirements of enzyme bates by the organised large scale tanneries, it is difficult to give any correct estimate for the requirements of the smaller units. It is likely that under the present conditions the total demand for enzyme bates for the entire leather industry in India may be of the order of 250 tons per year. As the Indian Tanning Industry is fast expanding, the potential demand for the enzyme bates is expected to be much greater. In the coming years, therefore, as the industry expands the demand for enzyme bates may be at best 400 tons per year.

With a view to manufacture enzyme bates in India and to stop their import, systematic researches were undertaken at this Institute to produce from cheap indigenous materials highly potent proteolytic enzyme which is the active ingredient of enzyme bates. In order to produce very active proteolytic enzymes from microbial sources, a number of micro-organisms were examined for proteolytic activity and the cultural conditions influencing the formation of proteolytic enzymes in certain molds of the Aspergillus group were critically investigated and the important nutritional factors which affect the formation of proteases in these molds were also studied[1] systematically. Methods were developed to culture these molds on cheap commercial media for the production of highly potent proteases.

As a result of these researches, three different processes [2-4] have been developed for the production of enzyme bates. The chief raw materials for the manufacture of enzyme bates by these processes are wheat bran, tapioca flour and commercial lactic acid. In the first process[2], the molds, *A. oryzae*, *A. parasiticus* or *A. flavus* were grown on a suitable culture medium for the optimum period of time and the enzymes isolated by water extraction of the molds and then by precipitation of the enzymes by ammonium sulphate. The finished bates have been prepared by mixing the isolated enzyme with wood flour and drying the mixture by warm air and finally adding different proportions of ammonium sulphate required for preparing different grades of bates for use in the manufacture of different kinds of leather. The grades are on the basis of proteolytic activity of the prepared bates as determined by the prescribed tests[5]. In the second process[3], the steps involved in isolating from the culture medium the enzymes secreted by the molds and the use of wood flour in the finished bates are dispensed with. The entire culture medium and the developed molds are mixed well, dried by warm air and finely powdered. Finally different proportions of ammonium sulphate are added In the third process[4] the molds are grown on the culture medium enriched with certain metallic salts and the very finely minced pancreas which is previously subjected to the necessary treatments for the conversion of trypsinogen to trypsin is mixed well with the entire culture medium and the developed molds, dried in a mechanical drier and finely powdered. To this blend of mold and pancreatic enzymes, which has been found to be more effective than either of them used separately, common salt and different proportions of ammonium sulphate and ammonium chloride are added.

Enzyme bates of two grades I and II have been prepared by the third process for the manufacture of glace kid and box sides and comparative studies of these bates and of the imported products Pancreol 5A and 3A, have been made with reference to their efficiency and proteolytic activity by laboratory tests[5] as well as by bating experiments on limed pelts. Our bates have been repeatedly tested not only in our tannery but also independently by several other commercial tanneries and quite satisfactory results have been obtained. A comparative study of cost of these products and of imported ones can be made only after starting production of these enzyme bates on a pilot plant scale. As the raw materials required for the manufacture of these bates are quite cheap and easily available and as the process of manufacture is also simple, it may be reasonably expected that these enzyme bates when produced on a large scale will be comparatively cheaper than the imported bates. We shall shortly start the production of these bates on a pilot plant scale to work out the economics and to effectively introduce them in the industry in place of the imported materials. There is immense scope for the large-scale production of enzyme bates in India.

Enzyme depilants are not commonly used for modern leather manufacture, although the possibility of using proteolytic enzymes for dehairing skins and hides was shown as early as 1910 by Rohm[6] in Germany, who developed for the first time an unhairing process, known as Ara-Ascher or Arazym process, in which pancreatic enzymes were used. Since then, a large number of patents have been taken by different workers on the preparation and uses of different types of enzymes derived from mold, bacterial, animal and plant sources. As a result of our systematic researches, three different processes[4], [7], [8] have been developed for the production and uses of highly active enzyme depilants for skins and hides. Our first process[7] makes use of the highly active proteolytic enzymes derived from the latex of certain plants *viz.*, madar (*Calotropis gigantea*). The second process[4] of enzymic unhairing has been developed making use of a blend of pancreatic enzymes and very active proteolytic enzymes which are produced from certain molds grown on a cheap and easily available medium. The third process[8] makes use of the amylolytic enzymes derived from certain germinated cereals, *e.g.*, ' Ragi ' (*Eleusine coracana*). It has been demonstrated that instead of using proteolytic enzymes, certain amylolytic enzymes also could be used for unhairing skins and hides. Burton *et al*[9] have reported that unhairing by means of certain mucolytic enzymes like diastase, pectinase, etc., is quite practicable. Recently, Cordon[10] found that eleven amylases of bacterial, fungal and animal origin brought about some hair loosening when used on salted hides.

There are, however, certain difficulties, for the commercial exploitation of the first and the third processes[7], [8] of enzymic unhairing, because the raw materials are not easily available and the cost of the processes may not be very low. In the case of the second process[4], the depilants can be produced at a low cost and the unhairing process is quite simple and can be commercially exploited.

There are certain advantages in unhairing by enzyme depilants. The time required for enzymic unhairing is much less than that required by the traditional liming process. The enzymic unhairing process, when properly controlled, can be applied with great success for getting the double action of unhairing and bating simultaneously in the same process. The unhaired pelt got by the enzymic unhairing process is quite clean in both the grain and flesh sides and has a bated feel and appearance. The hair recovered from the enzymic unhairing process is quite clean and not damaged as in the liming process. The enzyme depilants prepared can therefore be safely used for dewooling sheepskins.

There are certain disadvantages also in the enzymic unhairing process. The unhaired pelts may not have satisfactory swelling and the opening up of the fibre structure also may not always be satisfactory. The removal of natural grease from skins and hides in the enzymic unhairing process may not always be complete. These difficulties, however, can be obviated if the process is carefully controlled and if a suitable pre—or after treatment is given.

As regards our academic researches on the biochemical reactions of depilatory enzymes on the individual proteins isolated from skins and hides, the investigation[11] has thrown some light on the possible mechanism of enzymic unhairing and has confirmed the earlier findings of Burton (loc cit.) though Gillespie[12], however, has cast doubt on them. Our investigation[11] has shown that the skin mucoids are readily hydrolysed by the proteolytic enzymes with the liberation of amino-acids and by the amylolytic enzymes with the liberation of reducing sugars. Recently, Cordon (loc. cit.) also observed that some sugar was released during the course of enzymic unhairing of skins and hides by amylases but no direct correlation was found between quantity of sugar released and depilatory action. It appears, that the enzymic unhairing by proteolytic or amylolytic enzymes depends more or less on the hydrolysis and removal of mucoid constituents of skins and hides. Mucoids may be considered as some sort of protein—carbohydrate complex and exhibit both protein and carbohydrate functions. They are distributed throughout hides and skins especially at the epidermal corium junction and around the hair follicles. Naturally, when the mucoids are hydrolysed and removed, the hair-roots are weakened and ultimately the hairs become loose.

The literature on the mechanism of bating is quite exhaustive. A number of theories have been proposed from time to time to elucidate the bating reactions. No theory, however, has been universally accepted as explaining all the known effects of bating on the pelt and on the finished leather. A theory put forward by Bogaert[13] and Pickard[14] suggested that the chief role of a bate is to remove the epidermal debris and the keratinous proteins from the surface of the pelt. The removal or loosening of the scud is generally regarded[15] as the essential feature of bating. However there is no experimental verification of this theory, as keratin is usually not attacked by bating enzymes. Also a proteolytic enzyme is not expected to remove fatty matters and lime soaps. This theory has however not received full support.

Another mechanism of bating which was suggested by Rosenthal[16], Seymour-Jones[17], Wilson[18] and others [13 15], is the digestion and removal of elastin fibres. A critical examination of the elastin theory, however, shows that under the practical bating conditions, only very little amount of elastin is removed. Roddy and O'Flaherty[19] found the typical elastic tissue pattern in bated stock. It can therefore be concluded that the enzymatic action on elastin is not the main function of a bate.

McLaughlin *et al*[20] reported that one of the main functions of bates is the removal or disruption of reticular tissue. From the observations of Kaye[21] and Roddy and O'Flaherty[22] it would appear that the reticular tissue is quite resistant to the digestive action of the usual bating enzymes.

The digestion of the *erector pili* muscles has also been reported to be an important function of bating enzymes. Lloyd[23] and Kritzinger[24] agree that the partial breakdown of the *erector pili* muscles is one of the most important functions of the bate. McLaughlin *et al*[20] found that even after normal bating contractivity of hair muscles is still maintained. Anderson's observation[25] about extensive digestion of these muscles would apply only to overbated skins. Enzymatic action on the hair muscle alone may not be responsible for the silky grain obtained in bating and the other typical bating characteristics.

Lenk[26] explained the reaction of bating enzymes assuming that rennase is the active principle of enzyme bates. No specific enzyme 'rennase' however, was isolated or observed in pancreatic enzyme preparations. This theory was disproved by Anderson[27] who showed that skins could be satisfactorily bated with enzymes of zero rennase content but not with an enzyme of high rennase but low proteolytic activity.

Marriott[28] proposed a β-collagen theory to explain the mechanism of bating. Kuntzel and Pototschnig[29] refuted the β-collagen theory on the grounds that a rapdily swollen collagen fibre may be digested by trypsin, but if first neutralised, it becomes resistant again.

Recently, Green[30] proposed a new theory of the mechanism of bating. According to him, the main function of bating is to reduce the tendency of the leather fibres to stick together on drying. By the action of lime, the collagen is converted to progelatin. Green (loc. cit.) believed that the removal of progelatin from the pelt causes 'falling,' development of flaccidity, scud loosening and air-permeability. This theory, however; has not been supported by unequivocal experimental evidence.

The proper removal of interfibrillary proteins has been reported to be an important function of enzyme bates. Improper removal can adversely affect the quality of the finished leather. It is well known that albumin and globulin of the interfibrillary material are readily digested by the tryptic enzyme systems of bates. Schneider[31] reported that skin mucoids are also attacked by trypsin. The digestion of interfibrillary proteins by bating enzymes has also been stressed by Kritzinger[24], and Pickard[14].

Stiasny[32] reported that the mild peptizing action of the enzyme on the collagen fibres is the most important action of bates and the qualities of the final leather are dependent upon this reaction to a great extent. According to him [32], this action, which is a structural and chemical loosening of the collagen fibres, results in the properties of smoothness, and slipperiness of the grain, air permeability, finger impression and water expressibility of the bated pelt and suppleness in the leather.

Borasky and Rogers[33], showed that intact collagen fibrils are resistant to tryptic digestion, but alkali or acid swelling causes filamentation of the fibrils rendering them readily digestible by trypsin. According to them[33], bating merely removes non-collagenous proteins and any collagen degraded in prior beamhouse treatments. However, prolonged heating at 30°–37°C. also causes filamentation, hence overbating will cause a definite loss of hide substance.

From the above, it would appear that one single theory may not provide a suitable answer to this problem. Systematic researches in this direction have been undertaken at this Institute on the biochemical reactions of different types of bating enzymes with the various constituents of skins and hides under the practical bating conditions. It is hoped that the completion of these experiments may throw some new light on the complicated problem of the mechanism of bating.

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SOME TECHNIQUES FOR THE ENZYME BATE PRODUCTION AND THEIR USE

BY

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ABSTRACT

The factors influencing the production of enzyme bates from different sources and techniques for the production and use of bates have been discussed. The practical aspects of the bating process for the manufacture of different types of leather and the earlier and modern concepts of bating have also been discussed.

It is well known that bating is one of the most important and delicate procedures in the manufacture of leather. It is a key operation for the manufacture of soft leathers like glazed kid, glove leather etc., and hence an expert and experienced person having careful judgement for the operation is needed to conduct the same. To achieve the proper characteristics of bating when the pelts come out of the bating bath, the following tests will be quite helpful :

1. The pH of the pelt after bating should be below 8.0 and the pH of the bate liquor towards the end should be between 7.5 and 8.0.
2. The pelt should be thoroughly porous.
3. The scud should be easily removable.
4. Deep thumb impression should be retained showing that all resiliency is removed and the pelt is absolutely fallen and flaccid.
5. Adhering flesh should......be easily removable.

Earlier concept of bating : The earlier procedure of bating was to treat the pelt with warm infusion of animal dungs. When weak action was desired, fowl dung was used and the process was called bating. When a relatively stronger action was desired, especially, on goat skins, dog dung was the ideal bating agent and the process was called puering.

It was the classical investigation of Wood[1] which threw light on the action of these strange processes. He showed that the bating action of the unpleasant dungs was mainly caused by enzymes secreted by the bacteria present in them. He demonstrated that the dungs contained proteolytic, amylolytic and lipolytic enzymes. In 1898, Wood[2] prepared trypsin from dog dung by precipitating the aqueous extract with alcohol. To this enzyme he added ammonium sulphate and found that it acted as an excellent bate. In 1907, Rohm[3] patented the application of a mixture of a pancreatic extract and ammonium salts as a bating agent. At that time, it was not possible to control the process properly. Hence, the pelts treated in this way were liable to be underbated, overbated or even completely damaged depending upon the enzymatic activity of the bate liquor.

Modern conception of bating : In the old puering and bating methods, two actions namely deliming and enzymatic action proceeded simultaneously. The enzymes were secreted by the bacteria. The carbon dioxide and small amounts of organic acids formed in the fermenting liquors acted as deliming agents.

In modern practice also deliming and bating are usually carried out in one operation. Nowadays, a large number of bating materials are available. All the bating materials are standardised on the basis of their proteolytic activity. Two types of commercial bates are available in the market : one containing no deliming agent, the other containing deliming agents such as ammonium sulphate, ammonium chloride, boric acid or various combinations of these agents.

Enzyme bates from animal pancreas : The pancreas of pig, buffalo, goat, sheep and cattle are widely used for the manufacture of bates. The comparatively richer source for the proteolytic enzyme is the pig pancreas. The beef pancreas, however, is available abundantly in India and can be used. The pig pancreas weighs about 100 gms. whereas the beef pancreas weighs about 250 gms.

Throughout the manufacturing process of bates from pancreas, one has to pay most attention to the preservation of proteolytic enzyme system. The proteolytic enzymes in the pancreas are present in inactive forms, chymotrypsin as chymotrypsinogen, trypsin as trypsinogen, carboxypeptidase as pro carboxypeptidase. That is why the enzymes have to be transformed from the inactive precursor into the active form by suitable treatments. It has been reported[4] that, if 0.02 M. calcium chloride is added to the pulped pancreas, it will inhibit completely the formation of inert protein and the trypsinogen is quantitatively converted to trypsin.

In the manufacturing processes, an extract may be prepared from the minced glands containing the fully activated proteolytic systems. The enzymes can be absorbed on wood flour or precipitated by organic solvents, *viz*., alcohol, acetone or by high concentrations of certain salts such as ammonium salt. The enzyme precipitate may then be mixed with wood flour and dried. The final product contains wood flour, active enzymes and ammonium salts.

Enzymatic bates from Bacteria : The first commercial bate was prepared[5] from cultures of *Bacillus erodiens* in 1896, its trade name was "Erodin." Wallerstein and others[6 7 8] described the methods of growing bacteria for the manufacture of enzymes. Wallerstein[9] prepared enzymes by growing bacteria of the mesentericus or subtilis group. The cultures were absorbed on wood flour, dried and mixed with ammonium chloride.

Enzymatic bates from molds : For commercial enzyme production, molds are suitably grown on wheat bran medium and other ingredients, several species of mold have been suggested by various workers. A systematic study by Bose *et al*[10] for the maximum production of enzyme from microbial sources has revealed that *A. parasiticus* is the best source for the protease. The enzyme product is dried, powdered and standardized. Enzymes may also be precipitated from the aqueous extractions of the mold cultures and the bate may be prepared according to the methods previously described for pancreatic bates.

Enzymatic bates from other sources : The possibility of using papain as a bate has been suggested by a number of authors.[11] [12] [13] Enzymes prepared from fish viscera, pine apple, fig banana or mulberry have also been suggested[13] for the manufacture of bate but they have not yet found industrial application.

Merits and demerits of different sources of enzymes for bate manufacture : Many workers have tried to find out the comparative efficiency of bates, prepared from different raw materials. But no definite conclusion has been drawn. Eling and Lollar[14] have pointed out that both microbiological and pancreatic bating preparations have similar action. According to Moore[15], however, pancreatic enzyme has greater efficiency in bating then the bacterial or fungal enzyme. Our practical experience shows that pancreatic enzyme is superior to microbial enzyme in imparting the fineness of grain for the manufacture of glazed kid. Pancreas is used for many medicinal preparations. It is rather costly. Hence, molds, if grown on a cheap medium, can be used as a substitute. If a combination of both mold and pancreatic enzyme in suitable proportion is made, it will be an ideal bate for different types of leather. Both the enzymes have got ready action on globular proteins of the skin or hide in alkaline pH.

Use of deliming agent for the bate manufacture : The principal materials which a bate contains are a proteolytic enzyme, a carrier for the enzyme like wood flour and a deliming agent like ammonium chloride or sulphate or both. The deliming agents are used for the removal of lime and lime salts and to bring down the pH of the pelt to about 8.0 to ensure proper enzyme action. Practical experience shows that ammonium sulphate which is used as a deliming agent gives a firmer as well as fuller flanks leather. But if the pelts are not washed properly, insoluble calcium sulphate forms a crust on the grain surface of the pelt and hence creates trouble in the subsequent processes. On the other hand, if ammonium chloride is used alone as the deliming agent, readily soluble calcium chloride is formed. That is why it is still preferred by some tanners. It has, however, been reported [16] that a higher concentration of calcium chloride has a detrimental effect on collagen. Hence it is advisable to use both the ammonium salts in suitable proportion to get better results. The concentration of the deliming agent should be so chosen that it should have no denaturing or inhibitory action on the enzymes. As little as 0.1% ammonium chloride in the bate will activate the enzyme.

Mechanical agitation : Certain physical changes take place when the skin passes through the bating operation. Although it is always better to perform bating operation in a paddle for regulating temperature and for controlling deliming action and enzyme action, drum bating has also some advantages, *viz.*, (*a*) economy in handling goods since drum can be used for other operations also and (*b*) use of smaller quantity of liquors. However, when drum bating is employed, it is always advisable to stop the drum periodically to prevent the development of too much heat. It is always better to see that the drum speed should not be too high.

Effect of temperature on bating : At a low temperature, the bating enzyme has got very mild action. The activity of the enzyme increases markedly with rising temperatures between 15 and 35°C. and with great acceleration at 45°C., thereby causing increased loss of hide substance. Hence it is advisable to avoid temperatures higher than 38°C., in bating operation. In India, it may be better to follow overnight bating practice for the manufacture of glazed kid. In this case, during the night time, the bating enzymes will have slow and mild action on the pelt. The next morning, if the temperature is raised to 37°–38°C. the bating will be finished quickly without having any adverse effect on the hide substance. It is, however, necessary to add some bactericide to the bate bath in the beginning in order to avoid the growth of any harmful bacteria. Proper care must be taken in summer to avoid overbating. It is known that underbating is always better than overbating. During bating in a paddle, proper precautions must be taken in introducing the live steam into the bath as the pelts at that stage are very much susceptible to spoilage by heat.

Effect of pH on bating : It is well-known that enzyme actions are very specific in nature and are influenced by the experimental conditions *e.g.*, the nature of the substrate, enzyme concentration, pH, temperature etc. The same class of enzymes may have different pH optima on the same substrate. For instance, the protease pepsin has got optimum action at pH 2.5, papain at 5.0 and trypsin at 8.0 when gelatin is used as the substrate. The bating enzyme is a crude preparation and may contain two or three enzymes. The pH of the bate bath should be adjusted according to the optimum pH of the bating enzymes. A crude preparation of pancreatin is also a mixture of several proteolytic enzymes and has the optimum pH of 8.3. The optimum pH of the proteolytic enzyme derived from mold sources is usually between 8.0 and 8.5. Hence the deliming agent should be added in such a proportion that the pH of the bate liquor should be brought to the optimum pH range of the bating enzyme within a very short time. It is, however, better to avoid too much of deliming agents. Bates containing ammonium salts react with the calcium hydroxide of the limed pelt liberating ammonia and thus resulting in an alkaline (pH 8.3 to 8.5) solution

$$Ca(OH)_2 + 2\,NH_4Cl = CaCl_2 + 2\,NH_4OH$$

Concentration of bate : It is rather difficult to suggest any hard and fast rule regarding the concentration of bating material as there is always a good deal of variation in the quality of the stock and also in the previous processes. Some hard natured skins require greater concentrations of bating enzymes. For some soft skins like "Erode" quality goat skin, lesser concentration of enzyme is necessary. Roughly it can be suggested that 1.0 to 1.5% of bate is quite sufficient for bating goat skin for glazed kid manufacture.

Water-skin ratio : The proportion of water to skin is important in bating. If the water is less, there will be undue crowding and the skins will not open up properly. If water is too much the skins will float out and the enzymes will be unnecessarily diluted. It is better to maintain the ratio of skin to water close to 1 : 4 in the case of paddle bating and 1 : 3 in case of drum bating.

Use of old bate liquors : In most of the glazed kid tanneries in U.S.A. and U.K. old bate liquors also are used to get proper bating action within shortest possible time so as to finish the bating operation within the same day and to minimise the use of fresh bate thereby reducing the cost of leather manufacture.

In India, however, very few tanners use old bate liquors. In this country also, some quantity of old bate liquors may be used ; for overnight bating, however, this practice will be rather risky, because enzymes secreted by the bacteria present in the old bate liquors may have detrimental effect on the hide substance.

Uniformity of stock : In order to get uniform bating effect it is always better to select uniform stock. If hard and soft skins or skins of different sizes are mixed together and are subjected to bating operation, it is impossible to get uniform bating effect. Hence it is advisable to select the pelts before bating and grade them according to the size and nature of the skin.

Use of bates for different types of leather

Glazed kid : For the manufacture of glazed kid, bating operation is indispensable. The pelts are partially delimed and bated with 1–1.5% of bate based on limed pelt weight. Bating is done preferably in a paddle. The temperature of the bath is maintained at 37–38°C. and the pH of the bate liquor is adjusted to 8.2 to 8.5. The duration of bating may vary between 4 and 9 hours depending upon the condition of pelts. After bating the pelts are washed with warm water and scudded.

Calf skin : For the bating of calf skin some tanners prefer lower temperature (32–35°C.) of the bating bath. Sometimes a small amount of acid is added to the bate liquor in the beginning for maintaining the pH between 6.5 and 7.0. At this pH, enzyme action is greatly inhibited while deliming will take place. When the skin is fallen sufficiently, the pH is adjusted to 8.5 to 9.0 to reactivate the enzyme. Amount of bate required varies between 0.75 and 1.5 per cent on the pelt weight and the duration of bating also varies between 1 and 4 hours depending upon the condition of pelts.

Side leathers : For the manufacture of side leathers drum bating is preferred by most tanners since satisfactory deliming and bating can be accomplished in the drum in much less time than that required in the paddle. This may be due to a higher concentration of bate in the short float employed and an acceleration of the deliming action through greater mechanical pounding of the stock in the drum. The clearing of the grain without too much loss of fulness of the stock may be considered as the main objective for bating this type of leathers.

Fine glove leather : For this type of leathers increasing concentration of bate or longer bating period or a combination of both may be necessary. The skins should be delimed completely by extra addition of ammonium salts. For normal skins duration of bating is 2 hours. In some cases, especially, for very light skins, the drum may be run for 1 hour, shut down for $\frac{3}{4}$ hour and then run for 15 minutes more. In each case, the drum is drained off and the stock is thoroughly washed for $\frac{1}{2}$ hour to 1 hour. The exact amount of the bate to be used as well as the running and washing periods will vary depending upon the nature and type of skin used.

Vegetable tanned leather : For this type of leather only grain deliming is required so that a large amount of deliming agents and a small quantity of an enzyme are used only to clear the grain. In India, most of the tanners do not use bate for this type of leather, but, for the manufacture of cycles saddle leathers some tanners use about 0.5% of bate on the pelt weight to get a clean and characteristic grain.

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DISCUSSION

Prof. A. N. Mikhailov : Is it possible to make leather with enzymatic depilation only and without the complementary liming ?

Dr. S. M. Bose (C.L.R.I.) : Actually for all the three processes developed by us, subsequent liming is not necessary. The unhairing has been exclusively by enzymes and while this process takes 24 hours in Indian summer, it takes three days in Indian winter.

Prof. Mikhailov : Is the quality of leather quite good ?

Dr. Bose : Unhairing is quite satisfactory and the leathers produced therefrom are also good. However, it is upto the tanners to judge the quality.

Dr. S. K. Barat : Is a carrier for the enzyme essential for bating action of these bates ?

Dr. S. M. Bose : I would like to draw attention to the three processes that have been developed by us. In the first process, a carrier, *viz.*, wood flour has been used in the traditional manner. In the second and third processes, this material has been dispensed with and the entire culture medium of the moulds has been used in the preparation of bates. This would indicate that absorption of the enzyme on a carrier is not essential for bating reaction. If the enzyme alone is dissolved in water and allowed to act at the optimum pH and temperature, the same salts are obtained. However, practical considerations come in, for it will not be convenient to weigh accurately very small quantities in tanneries and control the reaction very carefully. So a bulky material which could be roughly weighed out is preferred by the practical tanners.

THE APPLICATION OF VERSENE FOR DETERMINATION OF CALCIUM AND MAGNESIUM IN SALTS USED FOR CURING HIDES AND SKINS

BY

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ABSTRACT

The determination of Ca and Mg present in salt samples used for curing purposes was carried out using EDTA method with Eriochrome Black T and Murexide indicators. 60 samples of salt from different parts of India were collected and analysed for their Ca and Mg contents. Caution has been advocated in the use of salts containing as high as 1.2% Mg for curing hides and skins which go into the production of quality leathers for its possible effect on the salt stain formation.

Complexometric titration methods are available for the determination of virtually all the elements of the periodic table and of organic materials and gases also. These methods have got potential applicability in leather research in the analysis of water and curing salts.

Of the various complexing agents like iminodiacetic acid, uranil diacetic acid, nitrilo tri-acetic and phenyl imino-diacetic acid, EDTA, diamino cyclone tetra acetic acid and their different derivatives, EDTA (versene) is one of the most widely used complexones. M. R. Verma[4], in an excellent survey, has classified metallic ions as those known to form definite complexes and those which are suspected of complex formation but whose composition has not been established and some of which are determined indirectly. The EDTA method has been widely accepted for determination of total hardness of water[1-4]. A. de Souza[5] and R. L. Desai and Singh[6] have established conditions for determination of $Ca^{++} + Mg^{++}$ in hard water and marine salts. The accurate determination of Ca^{++} and Mg^{++} especially the latter, in the water used for tanning and in the salts used for curing is of vital importance for the production of quality leathers because it is since long known that stains are formed after curing with salts of certain types. The origin of these stains has been the subject of controversies. There is a view that they may be of bacterial origin[7], but when the leathers are conditioned for the suitability of bacterial growth, no such stains are observed[8]. A. Kuntzel and co-worker[9] continued microscopic and other examinations of leathers subject to these stains and suggested that Mg forms a characteristic salt stain precipitate with blood fractions and non-collagenous skin components which get deposited in the fibre structure causing stains. The remedy suggested by them is the addition of poly phosphate, complexone or carbonate to the curing salt so that magnesium forms complexes soluble in water. In the present paper, an attempt is made to show the feasibility and elegance of EDTA method in studying the nature of salts of different origin in relation to their curing effects.

Of the many methods for detecting end point like indicator titration, high frequency titration, spectrophotometric and polarographic methods, we took advantage of the volumetric method utilising Eriochrome Black T for the combined determination of calcium and magnesium in $NH_3 — NH_4Cl$ buffer at pH10 and Murexide for that of Calcium alone as employed by de Souza *et al.* (loc. cit.) The wine-red colour formed by the weak complex of Ca^{++} and Mg^{++} with Eriochrome Black T changes to blue at the end point by the formation of a strong complex of EDTA with metallic ions at the specific pH value. The bright red colour of murexide complex with Ca^{++} is changed to blue violet at the end point.

Reagents required: EDTA was purified by precipitation from aqueous solution by the addition of alcohol. The filtered solid was dried at 100°C. overnight. A 0.1 Molar stock solution was prepared by weighing 37.2 gms. into a litre of double distilled water. The solution was again diluted further by 10 times depending on the necessity.

Eriochrome Black T: A 0.4% solution was prepared in methanol.

Murexide: A saturated aqueous solution was used.

Buffer: Equal volumes of 0.5 M NH_4Cl and NH_3 were mixed adding 20 ml. of liquid NH_3 of specific gravity of 0.88 which gave a pH of 10.

Experimental: To 25 ml. of the salt solution 15 ml. of NH_3 buffer were added and heated to a temperature of 45°C. and after adding 0.1 ml. Eriochrome, the titrant was run down from 5 ml. microburette till the colour was just changed. This gives the combined value for Ca and Mg. Another aliquot was used for Ca after adding 0.1 ml. of the indicator and 1 ml. of 5 N NaOH and diluting to the same volume.

Table 1

Estimation of calcium magnesium in marine salt

Sample No.	% Calcium	% Magnesium
	(On 0%	moisture basis)
1.	0.0412	0.03333
2.	0.05955	
4.	0.1525	0.6726
5.	0.1611	0.1760
6.	0.1515	0.5023
7.	0.1019	0.2737
9.	0.1089	0.3414
10.	0.1183	1.3770
11.	0.4997	0.0246
12.	0.1987	0.0834
13.	0.1391	0.1182
14.	0.6174	0.01739
17.	0.1436	0.3583
18.	0.00325	1.3620
21.	0.1518	0.6339
22.	2.4050	...
24.	0.1604	1.7520
25.	...	0.02662
33.	0.1158	0.0728
37.	0.1860	0.4369
44.	0.1379	0.4865
50.	0.1320	0.0053
55.	0.3958	Nil

Discussion : About 60 different samples were analysed using the above method, and the results are given in the adjacent table. The Mg content of different samples varies from 0.0100 to 1.7520% and that of Ca from 0.0032% to 0.5%. No specific difficulties were encountered except that in one case the combined value of Ca and Mg was lower than for Ca alone. This may be due to the impurities which interfere in the EDTA titration which, of course, are unlikely to be present in the salts. However, the nature of anomaly is under investigation. The limits of applicability of this method are 0.1 to 2.5 gm./100 gm. salt for Ca and 0.2 to 3.0 gm./100 for Mg.

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INSTRUMENTAL METHODS FOR ASSESSMENT OF LEATHER AUXILIARIES

BY

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ABSTRACT

Instrumental methods like spectrophotometry, electrophoresis, chromatography, polarography, nonaqueous titrimetry, etc., are coming into prominence for the characterisation, analysis and assessment of several leather auxiliaries. An attempt is made in this paper to deal critically with some of the techniques with special emphasis on the work carried out at the Institute and the future scope of these techniques.

Instrumental methods cover a very wide field ranging from spectrophotometry and chromatography to X-ray diffraction, electron microscopy and tracer techniques and most of these techniques are utilised in characterising leather auxiliaries. It is not possible in a short paper to survey exhaustively the applications of all the techniques. The object of the present paper is to deal with a few that are acclaimed to be important and useful and with which work has been initiated and is in progress at the Central Leather Research Institute. Instrumental methods generally surpass other routine and conventional procedures in rapidity, reliability and reproducibility.

Applications of a spectrophotometry

Spectrophotometry has come to stay as one of the most useful tools of analytical chemist. It comprises the visible, u-v and infra red regions and determines the absorptive capacities of materials at various wave-lengths. Since the absorbances are directly related to the concentrations and the maxima to specific chromophore groups, qualitative and quantitative interpretation is made possible.

The method of estimation of tannin by the official hide powder method has been known to be defective due to the dependence of the method on the environmental factors involved. The chemical methods for finding out the tannin content suffer from non-reproductibility, difficulty in detecting end-point etc. Hence arises the necessity for instrumental methods. The methods put forward hitherto have been rather indirect in the sense that first a standard curve is obtained with the hide powder method and the tannin content read from either the u-v absorbance of the unknown solution or the visible absorbance of the coloured ferrous tartrate complex[2]. A more direct method was put forward by Goldschmidt, for lignins, tannins etc.[3] which depends on the absorbances of phenolic groups in buffers of pH 10, and the phenolic content computed from the molar absorptivity maximum of model phenols. The study was extended to indigenous and other tanstuffs by Nayudamma *et al*[4]. But difficulty in correlation was experienced mainly because the primary units of the various tanning materials differ much and are not known precisely and the model compounds do not strictly correspond to the tanning materials.

Chromium has been determined in liquors and leather by the coloured diphenyl carbazide complex[5]. This method has been used in this laboratory after standardising the optimum conditions for determination of a fraction of micromole employed in chromatographic procedures[6].

Methods are also available in literature for determination of Al, Zr and Fe spectrophotometrically.[7, 8, 9]

Wherever a range of wave-length would suffice for the determination, cheaper instruments like colorimeter could be employed.

Diffuse reflectance values from spectrophotometer and the tristimulus colorimeter have been used as aids in standardisation of colour of leather finishes to eliminate as far as possible errors due to human judgment[10]. A simple device has also been described for measuring relative capacities.[12] A tristimulus colorimeter has been procured and studies on this very important problem of colour of finishes are proposed to be initiated at this Institute.

Conductometry

Conductometry is a simple technique whereby the resistance of the solution which contributes towards the conductances between two platinum electrodes is measured. The change in conductivity with the addition of the titrant gives when plotted characteristic results.

Thus conductometric titrations have been employed for the determination of various acidic groups in syntans.[13] The strong acids *viz.*, sulphuric and sulphonic, the weak acids like oxalic acid and carboxyl groups and the weaker acids of phenolic groups have all been differentially titrated by employing this tool. It has also been found possible to have some insight into the nature of the commercial syntans. Another useful application as standardised by Mathur[14] consists in determining the sulphate content in lignin sulphonic acid liquors.

There is also scope for employing this technique in the analysis of lime liquors. Preliminary experiments have shown that the sulphide and hydrosulphide are differentially titratable from hydroxide, chloride and carbonate.

Potentiometric titration technique

Electrometric titration is a very common and useful technique where change in potential is plotted against titrant added. In neutralisation reactions the technique is widely employed for determination of basicity of chrome liquors and for the salts and acid content of tan liquors. In the oxidation-reduction type reaction, the technique is used for determination of chrome content.

During the last decade, due to limitations in using water as solvent for titration because of its amphoteric nature, electrometric titration in non aqueous medium has been proposed.[15,16] This possesses considerable advantage in that the acidic or basic character of the substance is enhanced. Titration in glycol-butanol mixture has been utilised for determination of salts of weak acids in vegetable tanning materials.[17] Titration in aqueous medium to a pH of 2.7 or 2.8, gives only arbitrary values without any particular end point whereas non-aqueous medium gives unmistakable end points within an error of ± 5%. The method has also been found to be of immense use in the case of mixed extracts, tan liquors and spent liquors since the presence of water upto 5% does not interfere much in the sharpness of inflexions.

Another useful application of this non-aqueous titration technique as developed in this laboratory consists in evaluating the degree of sulphation in sulphated products like syntans and fat liquors,[18, 19] where the residual sulphuric acid is distinctly and differentially titrated from the sulphated products. The method can be easily adopted and applied in the industry manufacturing sulphated products.

One of the achievements of the application of non-aqueous titration technique consists in its application to fat liquors.[20] The fat liquors contain a mixture of SO_3Na group, OSO_3Na group, COONa group, COOH group and if unneutralised, SO_3H and free sulphuric acid. The determination of these different constituents especially the organically combined sulphur by usual chemical methods is time consuming and somewhat laborious. In one case the end point is also not quite sharp. Recently, an elegant method has been developed in this laboratory so that all these groups could be differentially titrated. The method consists in separating the inorganic constituents first and then titrating in glycol medium with standard acid, for OSO_3Na and COONa groups and with standard alkali for COOH and SO_3H or H_2SO_4 groups if any. The titration with acid when carried out in presence of Hg[illegible] acetate gives SO_3Na group in addition. The OSO_3Na group however is separately determined by hydrolysis with HCl and differentially titrating the acid sulphate formed.

Non-aqueous titration technique has also been used for determination of weak acids in tan liquors and non-complexed salts in masked chrome liquors.[21] Thus the potentialities of this technique seem to be unlimited. It may be hoped that in the near future a simple titration in non-aqueous medium alone may give the tannin content itself of natural vegetable tanstuffs since tanning action is primarily due to phenolic hydroxyl groups which are very weak acids.

Polarography

Polarography is one of the newest popular instrumental methods and has been applied successfully to organic and inorganic compounds. If the conditions are standardized so that the reaction at the dropping mercury electrode is diffusion controlled, then the current developed known as diffusion current is proportional to the concentration of the substance and the potential at half inflexion gives qualitative information. Thus Vlcek[22] obtained anodic polarograms of polyphenols and tanning compounds and showed the possibility of estimating tannins. The auto-oxidation products of polyphenols and tanning materials have been studied in this laboratory[23] and conditions have been standardised for the determination of the parent compound polarographically.

Polarimetry

Polarimeter is the instrument to measure the rotation of the plane polarised light. Glucose, sugar and molasses reduced chrome liquors can be examined by this technique for the excess of sugars.

Electrophoresis and chromatography

Electrophoresis is the technique used for separation of the ions in an applied electrical field, due to the different mobilities of the ions, the different charges or differences in particle sizes contributing to the separation. The technique has been used with advantage in the Institute for separation of the differently charged chrome complexes and the different constituents of the tanning materials. Continuous electrophoresis is also used for collecting the different fractions.

A paper of this type will be incomplete without reference being made to chromatographic technique. Particularly, the paper chromatographic method has been adopted in almost all the fields in scientific research as a valuable tool. The method is finding increasing application in the evaluation and determination of different constituents of indigenous and other tanning materials[24] and in determining the oxidation products like organic acids of glucose and sugar reduced chrome liquors.[25] Attempts have been made to use the technique with syntans also.

Thus it is seen that a variety of instrumental techniques can be used with advantage in the evaluation and assessment of leather auxiliaries. The field is very rich since instrumental techniques are extending their scope everyday and much of unexplored regions comes to light with the development of newer techniques.

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DISCUSSION

Prof. A. N. Mikhailov : Allow me to make some remarks about the colorimetric analysis of tannins. Tannins are complicated in composition. We see that the colorimetric method of tanning analysis will not solve the problem. We should try to substitute hide powder by other materials like synthetic polyamides which could be hydrolysed to obtain conditions similar to those in hide powder.

Mr. Sanjoy Sen (National Tannery Ltd.) : What is the effect of dilution on the method ?

Dr. D. Ramaswamy : Dilution does not contribute much error at the concentrations used, namely 10^{-2} to 10^{-4} molar solutions.

Mr. Sanjoy Sen (National Tannery, Calcutta) : It has been our experience that the colorimetric method for estimation of chrome was capable of 10% accuracy whereas in the chemical methods the error is less. What is the order of deviation in the present method ?

Dr. D. Ramaswamy : The maximum permissible error for any one of these methods is 5% and in our experiments this limit was not exceeded.

Mr. K. N. Nair (Laxmi Tannin Extract Factory) : Could tannin and non-tannin be determined by specific gravity alone ?

Dr. D. Ramaswamy : I believe there will be a lot of fluctuations and errors.

Dr. S. K. Barat (C.L.R.I.) : Raised some points regarding estimation of tannins.

Dr. D. Ramaswamy : By the spectrophotometric method as developed at present, it will not be possible to distinguish the phenolic tans from the phenolic non-tans. In a recent publication, I have suggested that the phenolic non-tannin content of tan liquors is absorbed to a major extent during treatment with the hide. Considering the errors in the hide powder method, introduced by the presence of non-tannin, it might be worthwhile to investigate this colorimetric method. The recent trend is to employ a non-aqueous titrimetric procedure.

Dr. S. K. Barat : The Indian Standards Institution, in its last meeting formed a committee to go into the question. As has been substantiated by Dr. Ramaswamy, unless the model compounds were got, the assessment of tan liquors would be difficult. The great advantage of the hide powder method is that it distinguishes tannins from non-tannins.

THE INFLUENCE OF DIFFERENT TANNING AUXILIARIES ON THE SWELLING OF HIDE PROTEIN

BY

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ABSTRACT

The swelling of hide or skin at every step of the manufacture of leather is an important factor determining some of the qualities of the resulting leather. The influence of some tanning auxiliaries (like surface active agents, lime liquors, tanning agents and the so-callee " non-swelling acids ") on the swelling of hide at the different stages of leather manufactud has been described. The formation of the shrunken grain in some tanbaths has also been discussed.

The hide protein, when placed in an aqueous medium, imbibes a certain amount of water and swells. Being amphoteric in nature the protein forms salts with acids as well as with bases, resulting in swelling by osmotic forces ; the degree of swelling depends on the pH of the medium and the presence of other osmotically active substances in the solution. The swelling is also influenced by the presence of lyotropic agents which may cause a breakdown in the structure of the protein. The swelling of hide is an important factor at every step of leather manufacture, since a definite degree of swelling may be necessary for imparting some desired qualities to the resulting leather. It is therefore helpful to know the effect of some of the important tanning auxiliaries on the swelling of hide and leather at the different stages of leather manufacture. In this paper some of the recent work done in this field has been described.

Soaking back and detergents : The first operation in which the hide takes up water is the soaking back of dried hides. The salt present in the cured hide helps the soaking back and swelling, but in case of hides which have been dried up too much, soaking back is difficult and some soaking agent may be employed to accelerate the wetting of the fibres and the dispersion of the interfibrillar proteins. The use of alkaline bath and of sulphides is already known and practised; of late however, surface active agents also are being used.

The rate of swelling of sun dried cowhide in absence and in presence of surface active agents under different conditions of pH, was studied by us using one cationic (triphenyl methyl ammonium iodide) and another anionic (sodium lauryl sulphonate) agent, using 0.05% solutions. The results indicated that excepting for the anionic type at pH 7.4 (*i.e.*, in a slightly alkaline pH) there was no significant increase in the rate of swelling, as well as in the actual value of swelling at the concentration employed.

The surface active agents may enhance the wetting of the fibres or the dislodging of interfibrillar proteins where there is not much gluing of fibres ; but in case of air dried hides with much of gluing their efficacy is doubtful. Experiments done in B.L.M.R.A. laboratory[1] using primary and secondary sulphated alcohols also point to the same conclusion. Since the detergents used now (*e.g.*, Mollaskal B,M.) are mostly anionic, cationic detergents of the quaternary ammonium type may be tried ; and it may be mentioned that apart from their detergent action they will be beneficial also in another respect, that is because of their bactericidal property.

Unhairing : lime and sharpeners : The swelling during unhairing in lime assumes a very high value due to the high pH (>12) prevailing. This is further influenced by other ions present in the system and has been studied by many workers.[2] Some interesting features alone may be pointed out here.

Swelling in lime is not only enhanced by alkaline salts like Na_2S which raise the pH of the liquor, but also by NaCl and $Na_2S_2O_3$ (hypo), contrary to our expectation based on the Donnan theory. Stubbings[3] has found that with a hide-lime liquor ratio of 1:4, at least 23% NaCl is required to suppress the swelling in the lime slurry ; below this concentration salt will only raise the swelling. Now, if the swelling is very high with the pH above 13, dissolution of the protein at the interface between grain and corium will occur causing a loose break of the final leather ; the irreversible breakdown of the structure at this pH will weaken the final leather and will make it less flexible. Dissolution of the hide substance by the bate will also be markedly increased.

Another interesting aspect in liming is the effect of shell lime on hide, this being very much used by the E.I. tanners. Since shell lime will contain besides $Ca(OH)_2$ certain other substances also (nitrogenous as well as salt), it will be mellower in action. Mitra and co-workers[4] found that while in stone-lime the swelling rises upto 18%, in shell lime it rises only upto 14.5% in the same time. Similarly in old lime liquor, the dissolved nitrogenous matters make it mellower by increasing the osmotic pressure outside. According to the above authors, this mellower action imparts to the pelt some properties desirable in the E.I. Kip manufacture.

The opening up of the structure : The irreversible changes in the structure of pelt by liming and bating, the splitting of the fibres and the opening up, were studied by us by comparing the swelling characteristics of unlimed and limed hide in one case and of bated and unbated hide in another. Swelling at any pH was found to be greater for the limed than for the unlimed hide and similarly, swelling for the bated hide was found to be greater than that for the unbated one. This shows that liming as well as bating open up the structure so that more liquid can be imbibed by the hide at any value of pH.

Swelling in tanbath : The swelling of the material in the actual tanbath assumes importance in so far as the filling up of the structure by tannin is concerned, as also in some other properties for the final leather, like thickness, firmness and the capacity to swell or rehydrate. A direct correlation between swelling and other physical properties has not been tried systematically and very little work has been done on the determination of swelling in the tan bath. While further work in this line is necessary to conclude anything of importance to the tanner, preliminary experiments carried out by us showed that (i) the swelling characteristics of dried leather are related to the swelling in the tanbath, and (ii) for the same type of tannage the degree of swelling of the leather is dependent on the degree of tannage.[5]

Bressler[6] observed that in case of tanning in willow bark liquor the higher the barkometer, the less was the swelling. Salts were however observed to increase the swelling. The swelling is of great importance in vegetable tanning as well as with any other high molecular co-ordinate active tanning agent, because centres of fixation are increased on swelling.[7] According to Anderson,[8] the greater the plumping in vegetable tan liquor, the greater is the firmness of the resulting leather. For chrome tanning Theis and co-workers[9] studied the effect of neutralising on the swelling of the chrome tanned leather and found that neutralising has the effect of slight rise in swelling. At a very high pH range, however, there is detanning and there is marked swelling. Nayudamma and co-workers[10] have also shown the great influence of salts on the fixation of formaldehyde by pelt and its effect on the swelling and shrinkage temperature of the resulting leather.

Astringency and the formation of drawn grain : The formation of drawn grain in astringent tan-liquors is yet another example of the importance of swelling in the tan-bath. While the wrinkles producing what is known as the "milled grain" are due to mechanical movement of the hides during tanning, the "Shrunken Grain" consisting of long parallel furrows is the result of swelling. The shrunken appearance of the grain, considered geometrically is not the result of a shrinkage of the grain with respect to the interior, but indicates that the area of the grain is greater than that of the next layers. Drawn grain is produced when a hide is placed in a bath containing tannin and an acid which can cause a swelling of the protein. The acid present slowly penetrates the grain, while the swelling of the grain is fixed by the tannin. The increase or decrease of area is influenced by the fiber weave in the different layers and how the fibres can adjust among themselves on swelling.

It has been shown by Quendt[11] that if a hide is first partly tanned and then put in a swelling bath shrunken grain will be produced but if it is first swollen and then put in the tan bath, shrunken grain will not be produced. It may be mentioned, however, that the production of drawn grain is not unique to vegetable tanning and may take place whenever the above conditions are satisfied.

The non-swelling acids : It will not be out of place here to indicate the most recent work done on the relation between the structure of organic compounds including dyestuff and the swelling of hide in systems containing them. Bergmann and co-workers[12] discovered in 1930 that naphthalene sulphonic acids do not swell the pelt. Following this, Otto[13] determined the degree of swelling and other properties of hide in various aromatics, low molecular and condensed sulphonic acids. It was shown that while benzene sulphonic acid has a strong swelling action, several others including polynuclear sulphonic acids do not cause much of it ; in fact, in some cases the swelling is reduced below the value in water. The property of these so-called "non-swelling acids" has been explained by Otto by considering co-ordinate forces and dipole interaction which seem to play a great part in the fixation of organic substances by hide. A comparison of the swelling action of four dye acids having 1, 2, 3 and 4—SO_3H groups respectively, has revealed that the greater the number of sulpho groups, the greater is the penetration and swelling and loss of co-ordinate linkage.[14] A dyestuff, in which one part of the molecule having a sulphonic acid group is joined to a nucleus not having any such group, has been shown to have a tanning action. That is why also the weakly sulphonated novolacs are fixed in much higher proportion than the strongly sulphonated novolacs.

The importance of the non-swelling acids in tannery work is evident and some of the applications have been discussed by Otto. For example, in deliming, if a non-swelling acid is used, it is easier to neutralise it completely, since we can add the acid in amounts that make the pH lower than the isoelectric point, without any danger of swelling the hide. A patent describes the use of 0.75% sulphoacid for deliming with no concomitant swelling.

In normal pickling, again, we have to add large quantities of NaCl to suppress the acid swelling. This salt is disadvantageous in several respects *viz.*, mineral tanning in present of salt gives a more flat or empty leather and less hide substance, than in absence of salt. In vegetable tanning in presence of salt, penetration is less and distribution of tannin not uniform throughout the hide. The use of non-swelling acids in pickling can eradicate these difficulties to a considerable extent. For industrial tanning also the use of non-swelling acid pickle influences the distribution of sulphur and gives a higher tensile strength. The fulness of chrome leather also is increased if pickling is done in absence of salt using these acids.

While the use of these acids in other cases has got to be systematically studied, we may say that the recent studies have opened a new line and helped a great deal in our understanding of the interaction between hide protein and other organic substances.

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DISCUSSION

Mr. G. S. Rama Iyer (C.L.R.I.) : I would like to know whether detergent concentration of more than 0.05% has been tried ?

Dr. S. Ghosh : Not in the present series of experiments.

LEATHER AUXILIARIES AND THEIR USES IN THE MANUFACTURE OF LEATHER

BY

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ABSTRACT

The dyestuff industry supplies a number of leather auxiliaries, used in dressing, dyeing, fatliquoring and finishing of leathers. Some of the auxiliaries can be used in production of fuller and better leathers. Fatty auxiliary agents also have been developed.

The various dyestuff manufacturers of the world have produced not only coal-tar dyestuffs of many kinds, but a variety of auxiliaries for use in the preparation, dyeing and finishing of different leathers. Practically all these auxiliaries are derived from or connected with some of the intermediate products used in connection with the manufacture of the various dyestuffs. These various auxiliaries find employment in the preparation, dyeing, fat liquoring or finishing of the substrate such as the basic leather substance employed in the process.

Some of these auxiliaries find their application in the dressing or tanning of skins and leather which are to be dyed. Most of the imported leathers are only just tanned sufficiently to enable them to be described as leathers, other are very poorly or inadequately tanned and such require a good retanning or even and entirely fresh tannage. Many so-called foreign basil tannages are partly or completely washed out with weak alkali. A light alkaline stripping reduces them to pelt. Even a thorough wash in water removes so much tannin that the remaining leather dries out harsh and tinny.

Such inadequately tanned leathers can be retanned with syntans, or one-bath chrome tanning liquors or even some of the rarer tanning products. Syntans have been used for many years for such a purpose ; in addition, these syntans always bleach the grain of the leather and remove salt stains.

A new type of syntan has been evolved in which the products are amphoteric, *i.e.*, possess two entirely oppositely charged groups, *viz.*, acidic and basic. A new syntan product links up with vegetable tanned leather by virtue of certain acid groups in its molecule. There are also some basic or amino groups which remain free and uncombined. By virtue of these uncombined basic groups, one can link up the leather with other acidic products, *e.g.*, tannins.

Thus one can retan or dress such vegetable tanned crust leathers with a pre-tanning synthetic tannin and subsequently with an astringent vegetable tannin in order to fill the leather and increase its weight and substance. This method has been used to fill loose and empty tanned kips with great advantage.

Still another application of a leather auxiliary is the use of suitable aluminium compounds. By retanning the lightly-tanned Indian leathers with basic aluminium compounds one can fill the looser skins, improve their feel and flesh so that it is practicable to convert them into suede leathers ready for dyeing into clothing suedes. The application of highly basic aluminium salts to the leather increases its firmness and is specially recommended for retanning loose or empty leathers such as certain types of Indian tanned sheepskins and also sheepskin tanned from domestic or New Zealand pelts. One can commence the retannage with a very basic aluminium salt and, if thought desirable, one can add some chrome tanning salt after a period with the aluminium salt. Leathers of a better nap and with a greater depth of shade are obtained by this process. It is recommended that they should be fat liquored with cationic fatliquors or with egg yolk.

It will be noted that the use of the above leather auxiliaries enables one to use looser and somewhat inferior types of skins than would normally be employed for such high-class suede leathers.

Certain leather auxiliaries are also useful in the production of sole leathers of fuller substance and better wear. One can retan the lightly tanned kips and buffalo hides with a pretanning syntan, such as contains amphoteric groups. The syntan attaches itself to the lightly tanned leather by virtue of the acidic groups, thus leaving the basic groups free and uncombined. It is thus possible to link on other acidic tannins, especially astringent tans, *e.g.*, crude quebracho with the free basic groups. The result is a fuller and firmer leather. In this way, loose and empty leathers can be filled and firmed. The loose and empty buffalo hide leathers can be improved in wearing qualities, Cheaper types of leather, *e.g.*, buffalo hide leathers, inferior grades of tanned kips, can be improved in feel and appearance, wear resistance and flexing resistance.

Fatty auxiliary agents have been developed considerably during the present century, especially during the past two decades. At one time, the only sulphated oils available were sulphated cod liver oil and sulphated castor oil. Sulphated cod oil was freely used in fat liquoring light leathers and its emulsion was much employed in oiling off heavy leathers. Sulphated castor oil was almost colourless but did not possess the lubricating properties of the fish oil product. Hence a sulphated cod oil was preferred to the sulphated castor oil. Then it was found that most of the sulphated cod oil products were darkened and stained leathers on which they were employed. This was particularly noticeable in the case of " white lining " leathers of which a considerable proportion used to be made. A new auxiliary agent was produced for fatliquoring and this was practically colourless. It was produced by sulphating " rosin oil," a wood product manufactured chiefly in America.

Sulphated rosin oil has been successfully produced and used, not only for fat liquoring, but also as an emulsifier for neutral oils, *e.g.*, castor, coconut and others. The sulphated rosin oil can be used to emulsify these neutral oils and also to drive them into the leather.

Sulphated fatty alcohols amides and esters can be used for the same purpose. They may be looked upon as synthetic or chemical products whereas the rosin oil is more closely akin to a natural product.

PROBLEMS FACING THE LEATHER AUXILIARY INDUSTRY IN INDIA

BY

Y. NAYUDAMMA AND V. S. PADMANABHAN

(Central Leather Research Institute, Madras)

ABSTRACT

The problems facing the leather auxiliary industry in India are dealt with.

The Leather Industry, one of the major industries of India, appears to have its origin in the Vedic age. It is quite reasonable, therefore, to suppose that leather trade also has been in existence right from those times, both raw hides and skins and tanned leather and leather goods figuring in our exports. With the occurrence of Industrial Revolution in the west, exports of tanned leather declined. However, we find a new trade—export of the partially tanned hides and skins springing up, the so-called East Indian Kips and Skins trade. Thanks to the inimitable quality of this type of leathers produced by purely empirical and indigenous methods, this trade is still flourishing. There is now a growing feeling that India should concentrate mainly in producing fully finished and high quality leather. It is in this particular context that the subject of the current symposium at the Central Leather Research Institute — Leather Auxiliaries—assumes prominence.

Whether by primitive methods or by the most modern methods, conversion of hide or skin into leather involves the use of a number of other auxiliary materials. The term " Leather Auxiliaries " is used to connote all those numerous materials that go into the making of leather (excepting, of course, hides and skins, the raw materials). The actual significance of these auxiliaries can be realised by reviewing the various stages in the modern practice of leather manufacture with particular reference to the types of materials used.

The freshly flayed outer covering of animals has to be preserved or 'cured' before it is used. The main ingredient used herein is common salt along with preservatives and insecticides like D.D.T., sodium silico-flouride, naphthalene etc. The first of the pretanning operations, is soaking wherein the cured material is soaked back and cleaned. While water is the actual soaking agent, several chemicals have to be employed alongside—surface active agents like Teepol for aiding penetration of water, chemicals like caustic soda useful in helping to soften the stiff skin or hide and preservatives to prevent bacterial damage during soaking. The soaked skin or hide is then "limed" to remove hair and other unwanted tissues and to swell the hide. This process involves mainly lime, to aid which are added sharpening agents like sodium sulphide, caustic soda etc., In the next process, the unhaired and fleshed hide or skin, now called the pelt, is delimed, *i.e.*, the excess lime is removed. Mineral acids, boric acid and certain organic acids and some acidic salts are used for this purpose. The pelt is bated if it is to be chrome tanned; the bating agents or bates used are mostly of pancreatic or mold origin and are enzymatic preparations admixed with diluents, ammonium salts, surface active agents etc. The next operation *viz*., pickling is optional, employed before chrome tanning and when the pelt is to be preserved, pickling is effected through a mixture of mineral acid and salt.

The subsequent process is the tanning proper. Broadly speaking, vegetable, mineral and synthetic tanning agents, formaldehyde and oils are made use of, either singly or in combination. As regards the vegetable tanning materials, it is to be noted that barks, twigs, leaves, pods, nuts etc., figure herein. Since it is only the leached out tanning material that is effective in tanning, attempts are now made to concentrate these leaches and get them in dry form as powder or as extract. It is also customary to modify these vegetable tannins, say by sulphiting or by bleaching, these processes involving use of chemicals like sulphite and oxalic acid. In the class of mineral tanning agents, we have basic chrome and aluminium and zirconium salts. In the preparation of first of these based on dichromate and sulphuric acid, reducing agents like glucose, molasses, saw dust, bagasse, vegetable tanstuffs, all come in handy as also inorganic salts like hypo. The synthetic tanning materials are all synthetic resins. These syntans can be tailored to suit their application and so, we have syntans of different types—auxiliary, replacement, bleaching, amphoteric etc., all derived from coal and coal-tar.

Coming now to the post-tanning operations, neutralisation comes into the picture only with mineral tannages and here, alkaline salts like sodium carbonate, borax and sodium salts of organic acids are utilised. Next follows the process of dyeing. Dyes of both acid and basic types (some of them quite specific for leather), mordants like bichromate and titanium oxalate, levelling agents for securing a uniform shade and chemicals for aiding quick and thorough penetration of dyes—these are the materials needed in this operation. Sometimes a change in surface characteristics as by light retannage—vegetable or syntan—is necessary. The dyed leather is next "fed" or "nourished" with oils, waxes and fats, this step being called fat-liquoring or oiling or stuffing depending upon the materials used. We find a whole series of compounds being used as constituents of the "fat-liquors"—sulphated derivatives of vegetable, marine and animal oils, and of fatty acids, alcohols and amides derived from these oils, solid fats and oils of vegetable, marine, mineral and synthetic origin and some emulsifiers ; the process of "sulphation" itself uses sulphuric acid, sodium chloride, sulphate, carbonate etc. It is, however, in the next operation, namely finishing, that quite an array of substances of different types is utilised : pigments of mineral and synthetic origin, binders like casein, glue and shellac, synthetic resins, lacquer binders, thickeners, fillers, dyes and colouring materials, emulsifying agents, plasticisers, special additives like waxes and so on. It may be also noted that chemicals like Epsom salt are used for filling leathers and that preparation of shoe polishes also uses up chemicals.

It may be thus seen that some hundred chemicals figure in preparation of leather running the whole gamut from common salt and heavy chemicals to fine organic chemicals. Actually auxiliaries worth about Rs. 60–70 million are consumed annually by the Indian Leather Industry, of which Rs. 20 million worth is imported into the country. This drain of money can be prevented only if self-sufficiency in these auxiliaries is achieved.

Let us now examine the position of the country, *vis-a-vis* the auxiliaries. Different varieties of salt-rock salt, sea salt and khari salt are used in curing. While the country may be self-sufficient in regard to this material, steps have to be taken to see that salt of the right grade is made available to the industry at comparatively cheap rates as much of our raw stock is damaged due to faulty curing. The preservatives and additives intended for prevention of salt stains should be of a sufficiently low cost. The researches carried out at the Central Leather Research Institute are of interest in that a suitable salt mixture overcoming the usual defects and effecting better preservation has been formulated.

The use of radio-active sands for curing, curing by drying in the sun with prior incorporation of wetting agents and dehydration using solvents are techniques deserving special mention. The Arnold paper cure method wherein paper impregnated with the preservative and salt mixture is pressed on to the flesh side of hide, thus effecting uniform transference of the reagents to the hide, seems to be suitable for our country in that it is a simple process.

With regard to the common material *viz.*, lime, about 50,000 tons are consumed, both shell and rock lime being used. Calcium carbide dust is yet another source of lime. The economics of preparing good slaked lime from any of these sources should be worked out, for the need to supply the tanner with good standard quality lime is there. As regards the adjuncts to lime, sodium sulphide (700 tons of which are estimated to be consumed annually) is made in India but it is reported that the prices have soared high quite recently and that the quality of the Indian product could be improved. The possibility of utilising barium sulphide as a substitute for sodium sulphide, certainly merits examination. Sodium hydrosulphide is preferred as a sharpener in other countries. At present, this material is neither manufactured in India nor imported. Researches at this Institute have indicated electrolytic methods to be useful for preparing this. Feasibility of doing this on a commercial scale as also that of manufacturing dimethylamine need to be investigated. The latter compound is useful as an unhairing agent in the preparation of certain special types of leathers. In this connection, some of the crude methods of unhairing prevalent in the country may be mentioned *e.g.*, utilising madar leaves. By a thorough study of the scientific principles underlying this process, the bad odour associated with the method could be eliminated and the method utilised by the cottage industry tanner. By preparation of depilants and bates from such indigenous sources, the present import of 100 tons of bates could be greatly reduced, if not stopped. Experiments carried out at the Central Leather Research Institute have demonstrated the utility of such indigenous oates and the Institute is in possession of the technical know-how for the manufacture of these. An intensive study of the Elangaram and Malni processes used for deliming, would be instrumental in evolving cheaper and perhaps better methods.

The situation with regard to the mineral tanning agents is not unsatisfactory for the country is rich in the basic materials needed for these. However, there is scope for development as for example, in the preparation of chrome tanning agents with masking additives incorporated in them and in the use of waste materials like sugarcane bagasse, spent tan liquors and of vegetable tanstuffs like didi-divi not very popular in the industry.

The chrome vegetable combination tanning extract, thus obtained by using vegetable tanstuffs for reduction of dichromate is remarkable in that it imparts the desirable properties of both chrome and vegetable tannages. Other similar combinations, chromium-aluminium, chromium-iron, chromium-aluminium-iron could be utilised for getting desired combination of properties. Processes have been developed at the Institute for the preparation and utilisation of such extracts.

The intensive researches carried out at the Institute have resulted in the preparation of basic aluminium salts. These could be used with advantage for preparation of white leathers and tanning reptile skins and in the manufacture of upholstery leather and the like.

By far the vegetable tanning industry is the biggest branch of the Indian Leather Industry. A variety of tanning materials, indigenous to the different States like avaram and babul are used in the cottage and small scale tanneries. Some are in scarce supply or getting to be too costly. A good amount of wattle bark and extract (30,000 tons) costing Rs. 10 million is at present being imported annually. Trials conducted at this Institute have shown that over 15 different materials are promising substitutes for the imported tanstuff. The co-operation of the Forest Departments of the various States is being sought to assess the availability of these promising indigenous materials and for steady supply of these to the tanning industry through organised plantation. It is estimated that over 30,000 tons of barks other than wattle are used. Myrobalan, an equal quantity of which is utilised, is available in plenty in India and there are three factories manufacturing its extract. As and when the potential resources are fully assessed, the indigenous materials could be converted into extracts, either alone or in blends. As has been demonstrated at the Institute, some of these materials like goran and divi-divi which though available in large quantities are not popular in the trade on account of certain undersirable properties, could be utilised when these defects are overcome by suitable chemical modifications.

About 150 tons of synthetic tannins are reported to be imported annually. While the importance of this type of tannins cannot be over-emphasised, it may be remarked that indigenous materials like rosin could be profitably used for this purpose. The Institute has the technical information needed in this direction. Ligno-sulphonates, waste products from the paper industry, constitute when modified, promising tanning agents, as has been shown by work in the Institute. Polymeric materials based on hexamathylene tetramine also have been shown, through work carried out at the Institute, to be useful for tanning, retanning and filling purposes. Complexes of resorcinol with hexamine have proved to be useful in improving the quality of indigenous vegetable tanned leather when used in retannage.

India abounds in a variety of oils—vegetable and marine. The fish oil that is at present available is not of good quality. So, if the fish oil industry of the West Coast is well developed and the quality of the product improved and standardised, then the tanners' requirements could be easily met. The annual consumption of fish and vegetable oils by the Leather Industry is placed at 4,000 tons and of tallow at 1,000 tons ; all of which is imported. As regards the fat-liquors, the investigations made at the Central Leather Research Institute have shown how certain non-edible vegetable oils could be used for this purpose after " sulphation." This would result in cutting down imports of fat-liquor.

The establishment of refineries in the country is a great step forward for petro-chemicals are slowly making their way into the Leather Industry. Mineral oils used in fat-liquors, some of the solvents for finishes, higher alcohols and waxes could be obtained from these. Here again existence of oil fields within India would be an additional advantage.

A number of heavy chemicals are needed by the Leather Industry. The position with regard to these appears to be satisfactory for they are produced in India, *e.g.*, sulphuric and hydrochloric acids, Glauber's salt, sodium dichromate, soda ash, sodium bicarbonate, caustic soda and ammonium chloride. While figures for actual consumption of these are not available for all, it may be taken that 1,500 tons of sulphuric acid and 1,200 tons of dichromate are required.

It is with respect to the supply of organic chemicals and solvents that the Industry has to depend entirely upon imports. We have no organic chemicals industry and it is here a beginning has to be made, for all the syntans, several of the finishing materials, emulsifiers, wetting agents etc., are derived from this. Several of the basic chemicals figuring in this organic chemicals industry are obtained from coal-tar and so a coal-tar and coal bye-products industry has to spring up for then only would it be possible to get our requirements locally. The establishment of such industries is vital not for the Leather Industry only but for the Plastics Industry also. Some of the polymeric products thus obtained are very valuable, for their incorporation into leather results in improvement in the quality of leathers. It may be mentioned *inter alia* that it is time that imports of chemicals like formalin at least are completely stopped.

Finishing occupies a very important position in the preparation of good and high quality leathers. In view of the fact that the majority of Indian Leathers are prepared from bad hides, its importance is further increased. Several of the materials used here are specific so far as leather is concerned. Pigments are available locally but the quality of the pigment finishes could be further improved. As for nitrocellulose lacquers, they are being produced locally but the quality has to be improved. Some of the imported binders could be advantageously replaced by suitable modification of indigenous materials like shellac and rosin. The improvement in the quality of Indian manufactured casein would be profitable. Attempts have also to be made to see whether finishing operations could be simplified so that the finish could be applied with a brush. Formulation of a finish suitable for this coupled with this simpler method of application would be a great boon to the small scale tanner who could avoid going in for costly equipment. Some amount of success has been achieved at the Central Leather Research Institute in this direction and further work is in progress.

As regards dyestuffs, there are plans for the development of this industry with the implementation of which the 150 tons of dyes required by the Leather Industry annually would be available locally.

Yet another direction is which imports could be stopped are the waxes—natural and synthetic. The attempts at exploiting sugarcane wax, a product going to waste at present by chemical modification will soon make this possible. These waxes are needed for preparing shoe polishes and the like.

A consideration of leather auxiliaries would not be complete without dealing with tanning machinery which are at present being imported. Attempts could be made in getting local engineering firms to manufacture against specific demands. The same is the case in regard to machinery for footwear and leather goods manufacture. Frames, zips etc., which are needed in this field, could be profitably manufactured using machines consuming only a little power, on cottage and small scale industry scale. The import of glazing glass cylinders and embossing plates could be avoided ; artistic talent for designing on metal is available in plenty in the country. Attention may also be given for developing machines suitable for small scale and cottage scale tanneries.

In addition to the materials mentioned above, other chemicals such as germicides, preservatives, disinfectants, wetting agents and adhesives find use in making leather and these are at present being imported. Preservative such as paranitrophenol, parachloro-meta-cresol could be made in India. As for wetting agents, there is scope for the preparation of these from the vegetable oil and the mineral oil industries existing in the country. Adhesives made from latex and polyvinyl acetate prepared in the institute have been found to be promising.

It may be seen from the above that a large number of the auxiliaries are required in comparatively small amounts. The development of the industries supplying leather auxiliaries would have to be on the following lines :

(1) In the case of materials available locally, standard quality of these will have to be ensured as also a reasonable price.

(2) Several of the indigenous materials could be advantageously utilised as substitutes for imported ones, possibly with a little modification.

(3) Certain vital industries have to be started not only from the point of view of Leather Industry but also for the sake of industrial progress of the country. While initially, the demand for the products of the newly started industries may be low, in course of time, with expansion of Leather Industry, the consumption is bound to increase and hence these industries would have a bright future. The need for creating markets for the finished leather and leather goods is of course there. Since starting of large scale production of chemicals required in small quantities may not be economical, attention will have to be bestowed on preparing these at cottage industry level.

Progress in the Leather Industry is intimately linked with self-sufficiency with regard to these auxiliaries. Actually, high quality leather can be produced only by employing these, the more so in the case of a country like ours, where the raw materials themselves are far from satisfactory. Therefore, the need for starting Leather Auxiliaries Industries does not call for a reiteration beyond saying that by stopping the imports and preparing these locally, the potential value of the Indian Leather Industry would be nearly doubled.

It is sincerely hoped that the discussions and deliberations of the Symposium held at the Central Leather Research Institute will pave the way for the progress of the Leather Industry.

LEATHER AND OTHER ALLIED INDUSTRIES IN NEW MYSORE STATE

BY

N. R. KEMBHAVI,

(*Hubli*)

ABSTRACT

A plea is made for developing the leather industry in the New Mysore State, along with the other allied industries producing bone meal and tallow.

'Leather Industry must Thrive' so said the Executive Secretary of the ECAFE Mr. C.V. Narasimhan, in his address at the fifth meeting of the Working Party on Small-scale Industries and Handicraft Marketing at Madras on June 17th, 1957. He also gave reasons for this. ' This Industry and so many industries could be established profitably in the Mysore State.

Prof. M. S. Thacker, Director-General of the Council of Scientific and Industrial Research said in the same meeting that the Indian Government was willing to give all the facilities available at the Leather Research Institute in Madras for research and training and disseminate information on the economics in production, cost, standardisation, and quality control of products, and, also promotion of marketing potentialities of this and other small scale industries in foreign countries.

The two letters published in the Readers' Forum of the Deccan Herald regarding "Tanneries in Mysore' by Mr. Rajapatel, Gulbarga and the other 'Help essential for Mysore Kip' by Valli Iqbal Ahmed tell the present unfortunate position of this industry in our State, though, in fact, this industry is one of the major industries of our State having all the natural advantages for being established on sound economic and quality basis. Such establishment will be profitable to the persons organising it, the State Government and also to the Central Government. This will not only give scope for earning more, to thousands of persons who have hereditary skill in developing this industry but also provide more facilities for improving their skill in preparing quality goods of the standard required by foreign countries and earn more money thereby.

The development of this and so many other industries is possible only through scientific researches getting technical knowledge or know-how, mass-scale production, finance for buying raw materials very cheap and by flooding our markets with the finished products.

Under such circumstances, development of our industries is not possible without Government help, financial and technical. Given this, it is certainly possible because we have all the natural advantages of raw materials available in abundant quantities enough and to spare for export and thus earn our much-needed foreign exchange.

For all this, this Industry will have to be developed on more scientific and economic basis, along with other allied industries such as belong to bone and bone-products, edible and industrial tallow from slaughtered and dead animals. Our country has the biggest cattle population in the world. Full use of the waste materials and by-products obtained in the process of manufacturing of quality goods, Tanning-extract from myrobalan, babool, *taravad* or *honnawari* bark, and the bark of many trees in our huge forests could be made. A solvent Extraction Plant for recovering oil from oil-cakes from the oil mills such as Groundnuts, Castor, Karanja or Honge and Neem and Maroti and waste fish and fish manure could be set up and the oil supplied to industries such as Soap, Textile, Leather etc., the deoiled cakes very rich in Nitrogen, could be used for preparing manure-mixtures or fertilizers on Nitrogen, Phosphorous and Potash basis (N.P.K.) along with the waste materials so obtained in the leather industry. All this will give 30–60 per cent more yield of our foodgrains and cash-crops than what we are getting now, as is done in all the advanced countries where the yield of these crops is 100/200 per cent more than in our country. Obviously, this will not only solve our food problem but will enable us to export to foreign countries earning Foreign Exchange for balancing our Export-Import trade.

It is in this respect, a scheme has been submitted to our Government and their reply is awaited to enable to start work.

AUXILIARIES FOR LEATHER MANUFACTURE

BY

H. LOEWE

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ABSTRACT

By leather auxiliaries such substances are meant which when applied in small quantities during leather manufacture, influence the processes and the end products in a favourable manner.

From the chemical point of view these can be classified into the following heads namely :

(1) Those that give complexes with metal salts.

(2) Ionic products.

(3) Non-ionic products.

The first class of substances finds application in influencing the course of chrome tanning and in the removal of iron and lime stains in vegetable tannage.

Ionic products can be classified once again into acids, bases, anionic auxiliaries and cationic auxiliaries. Acids are used for the simple process of deliming, bases in liming as sharpeners and anionic and cationic auxiliaries for dyeing and as wetting agents. Syntans of amphoteric character are used for pretanning in vegetable tanning and retanning of chrome leather.

By auxiliaries are meant such substances which when added in small quantities during the manufacture of leather, influence the process as well as properties of the end products in a favourable manner.

From the chemical point of view, these substances are compounds of very divergent compositions. In the market, one finds a large number of these auxiliaries under the most varying fancy trade names. It appears, therefore worthwhile to classify these products on the basis of the effects they produce ;

One can differentiate two groups of auxiliaries :

1. Complex forming auxiliaries
2. Surface active auxiliaries

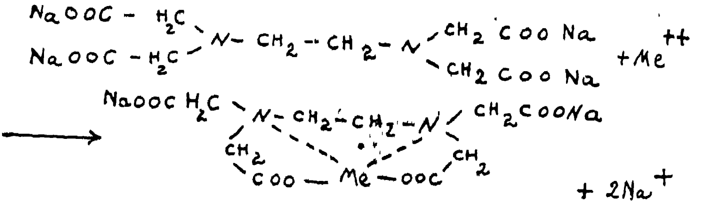
(Surface active auxiliaries are subclassified into ionic and non-ionic.)

The first group is of particular interest for checking the mineral tannage, in particular, the chrome tannage. The products used in practice for building up complexes are frequently salts of carboxylic or hydroxycarboxylic acids less frequently the carboxylic acids themselves. As inorganic complex building compounds, sulphites and phosphates are used. Today a series of complex-formers are at the disposal of the tanner, for all stages of the tanning process thus enabling control of the process in any desired manner, when basic metal sulphate or chlorides are used. In the chrome tanning very often liquors are used which are obtained by the reduction of bichromates with organic substances such as glucose ; by a suitable controlling of the reduction process one can obtain to some extent complexed chrome salts through formation of organic acids. In this instance, the quantity and type of the corresponding complex-forming acids depend on the course of the reduction process which is difficult to control. A sufficiently quick and accurate analytical control of the liquors so manufactured is very difficult to achieve. Because of this reason, one starts today with definite basic chrome salts and adds the complex substances in suitable quantities and at the right time during tanning. In the addition of these complex-building substances, it is to be noted that the anions of weak acids enter the complex quicker than those of stronger acids. Therefore, strong acids or their salts are added in the beginning of the tannage and weak acids towards the end. The quantities added should be so calculated that they only mellow the affinity of the chrome salt but do not reduce it drastically. In the first instance, leathers with a smooth grain, good fullness and with an uniform distribution of the chrome in the entire cross section are obtained whereas in the second, only flat and empty leathers will be obtained. Definite methods of application are available for these various complex-building substances, found in the auxiliary industry which are also frequently known as masking agents. Of particular interest are the complex-builders of aromatic nature such as the phthalic and sulpho-phthalic acids. (DP 891440 Inventor : Otto, Krzikalla/BASF). In this instance a particularly stable building up of the chrome complex takes place through increased dipole affinities which operate between the aromatic nucleus and the peptide groups of the collagen.

By the application of sufficient quantities of these complex-builders one succeeds in obtaining chrome leathers fast to sweat which is of special significance in the manufacture of *Prothesen* leathers. Also the tanning effect obtained with the high basic aluminium salts can be improved by the application of suitable complex-forming substances. The tanning with basic ferric salts is altogether made possible only through the application of complex iron salts, which on the one hand check an over-hydrolysis and so regulate the affinity and on the other bring about stable binding with collagen. In this manner, Redox reactions which can lead to a reddening of the leather are eliminated. In this case as well aromatic complex-building substances are particularly valued.

These complex-forming substances are of interest not only for retarding the tannage with metal salts, but also, whenever necessary, to remove the metal compounds vitiating the tanning process, such as iron and calcium salts.

Thus, ethylene diamine tetra acetic acid, is capable of satisfying four coordinate valancies and thus eliminate the iron stains occurring during vegetable tannage or on vegetable tanned leather. The above mentioned reaction can be illustrated in the following scheme :



It is to be noted that the compound mentioned above builds up very stable complexes both with divalent and the trivalent iron.

Certain synthetic tanning materials contain similar complex-building groups so that iron stains traceable to the application of water containing iron in tanning can be removed from the beginning.

Also lime stains can be removed with the help of complex-builders. With normal strong acids forming soluble calcium salts, it is not possible to remove the lime stains, but in contrast to this, the sulpho-phthalic acids, whose carboxyl groups are capable of satisfying the co-ordinate valancies of the calcium form easily soluble calcium salts.

The ionic auxiliaries are to be classified under the following groups :

Acids ;

Bases ;

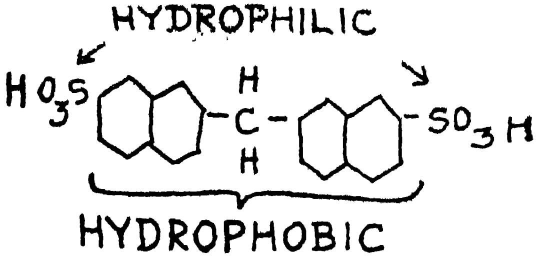
Anionic Auxiliaries ;

Cationic Auxiliaries ;

Amphoteric Auxiliaries.

The simple acids such as sulphuric and hydrochloric are used to control the acidity of the pelt, mostly prior to a mineral tannage. These acids swell the pelt through (charging) loading the collagen chain if their dissociation is not reduced by sufficient quantities of salts. But non-swelling strong acids suitable for pickling also are available. Their particular behaviour depends on their aromatic nature. Dipole forces come into play between the aromatic nucleus of the acid and the peptide group of the collagen while electrovalent bonds occur with the oppositely charged basic groups of the collagen. In this manner, a cross linking of the collagen chains takes place which however weak it may be, is sufficient to prevent any swelling effect. The strength of such cross linkages is, however, too weak to bring about a tanning action. An acid of this type, which has a high dipolar activity is the sulpho-phthalic acid, mention of which was made already. It forms easily soluble calcium salts and is therefore suitable also for deliming, where, even when overdoses are used no swelling effect can set in. (DP 882889, 3–10–42 Inventor : H. Loewe and H. Krzikalla, BASF). In de-liming with these acids, the complexing properties mentioned earlier are of particular significance. When sulpho-phthalic acid is used in the pickle either alone or with sulphuric acid, the quantities of salt usually applied in the pickle can be reduced. By this method the pelts are not dehydrated so strongly as in the case of a normal pickle for tanning and this leads to a fuller leather.

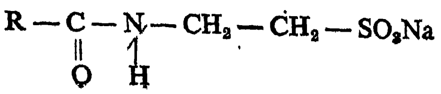
Strong acids are capable of tanning if their molecules are sufficiently large and a great affinity for collagen exists by increase in the reactive points. The condensation product of two molecules of beta-naphthalene-sulphonic acid and formaldehyde is thus a tanning acid :



The formula of this condensation product shows that such a tanning material has a structure similar to a surface active compound ; it is, therefore, understandable when this synthetic tanning material has the properties of a dispersing agent and so is able to dissolve phlobaphenes. Synthetic tanning materials of this structure are remarkable auxiliary tanning materials which quicken penetration, prevent the formation of sludges and work as bleaching agents. Since they contain no phenolic groups they do not give any coloured compounds with iron. Because of this, they are suitable for dissolving iron and to remove the stains on leather caused by the reaction of iron.

Among alkaline auxiliaries amines are of particular significance. Amines swell hides and pelts only to a very little extent. This property is made use of in the soaking of dried hides. In contrast to the accelerated soaking with strong alkalis, these amines do not bring about any deformation of the collagen chain and therefore one obtains leather with a smooth and fine grain. Also loose grain structure is eliminated. When applied in liming, the amines minimise the strong alkaline swelling, and further, impart to the lime the good properties of an old lime without the disadvantages of too strong an attack on the hide substance.

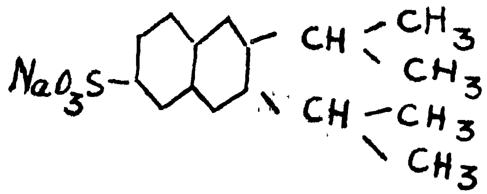
Anionic compounds are widely used auxiliaries which find application in all phases of leather manufacture. The hydrophobic part of these auxiliaries are built on hydro-carbons which are mostly aliphatic, often also aromatic and sometimes of both aliphatic and aromatic nature. The hydro-philic parts are built from sulphuric acid in most of the cases, in which the sulphur is bound either directly to carbon (as in sulphonate) or linked to the hydrocarbon through an oxygen atom as in sulphates. The latter type of linkage similar to that of esters is present in fatty alcohol sulphates. Sometimes, they are derived from fatty acids also in that the carboxyl group is blocked through substitution with ketoimid group, giving rise to compounds of the following composition :



$$R - \underset{\underset{O}{\|}}{C} - \underset{\underset{H}{|}}{N} - CH_2 - CH_2 - SO_3Na$$

R — hydrocarbon

in which R denotes an aliphatic residue. As example of an aromatic-aliphatic compound, which is very active as a wetting agent, the sodium salt of di-iso-propyl-naphthalene-sulphonic acid can be given. This compound possesses the following formula :



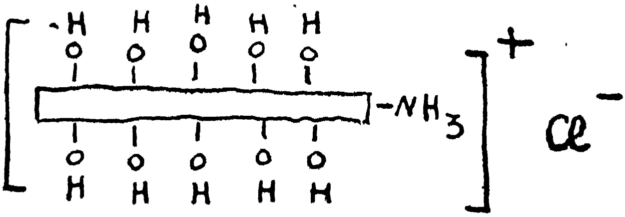
Surface active agents of this type are applied in all phases of leather manufacture. The fact that these become bound to the hide, pelt or leather, when they possess an opposite charge is to be noted. In this case they become inactive and lose their typical properties such as wetting, emulsifying and dispersing on the one hand, and on, the other they also reduce the number of cationic charges on the processed material. The charge of the material that is processed is again a function of the pH value of the water medium in which it is processed. For example, when it is desired to degrease pelt containing fat, with anion active emulsifying agents, it can be possible only at a pH of above 5 which is the iso-electric point of the pelt. In practice, this signifies that the anionic emulsifying agents will be capable of being active in liming. In the case of pickled pelts the charge of hide protein is predominantly positive ; when one applies anionic emulsifying agents to de-grease these materials they will be inactive since they become bound to the collagen. When anionic wetting agents are used for soaking hides they give certain particular effects besides that of wetting. Of particular interest is the action of those wetting agents which contain an aromatic nucleus. These auxiliaries have a remarkable hydro-tropic effect. This hydro-tropic effect is due to the reaction between the peptide group of the collagen and the aromatic nucleus brought about by the dipole forces. Through this affinity the hydrogen bonds of the collagen chain are broken and the freed peptide groups bind themselves with the aromatic nucleus of the wetting agents. The ionising hydro-philic groups of the wetting agent take up the water molecule and bring it inside the collagen chain. In this manner the collagen swells and its structure becomes loosened. Aliphatic wetting agents also show a hydro-tropic effect though to a substantially smaller extent (*vide* G. Otto " Das Leder 1957, 8, 100). The hydro-tropic effect of wetting agents is particularly important when these are used as soaking agents for dried hides. By drying the hides the peptide chains in the collagen are brought nearer, resulting in additional hydrogen bonds which harden them. By the addition of a weakly hydro-tropic material these hydrogen bonds are broken and the collagen is brought back to its released condition.

Among surface active compounds which have a predominantly aromatic character are also those which are applied as levelling agents in the dyeing with anionic dyestuffs. Neutral salts of auxiliary and replacement tanning materials are used for this purpose. They compete with the dyestuffs for the same active spots in the leather and slow down their uptake. By such a reduction of the affinity, a levelling action is achieved. When these auxiliaries have a complex active group as well, they are particularly suitable for chrome leather and impart an elastic grain. (D.P. 802071/G.Otto, BASF).

Of more recent origin are the cationic auxiliaries which are used in ever increasing quantities in the leather manufacture. Heterocylic compounds similar in character to hexamethylene tetramine, are the much used tanning fixing materials. As surface active cationic auxiliaries, salts of amines or quaternary ammonium compounds find application. In many instances when the hydrophobic parts of these compounds consist of a long chain of hydrocarbons, these auxiliaries have a fatliquoring effect. Products of this nature are used mainly in the dyeing and fatliquoring of leather. In dyeing one uses these materials in such cases where it is desired to increase the affinity of the anionic dyestuffs to the leather. This is for example the case, when chrome leather is retanned with vegetable or synthetic tanning materials. Also when it is desired to prevent the full penetration of the dyestuff in the brush dyeing of glove leather with anionic dyestuffs, a pre-treatment of the leather with cation active auxiliaries is of advantage. The effect is produced by changing the charge conditions of the leather surface in such a way as to bind the anionic dyestuff just on the outer surfaces of the leather. The sweat, water and washing fastnesses of dyeing with anionic dyestuffs are increased remarkably by an after-treatment with suitable highly active quaternary ammonium compounds. (P.A. B-37113 IV c/8 m Inventor—Otto/Gehm/Schuster, BASF). Such an after-treatment is of particular interest in the dyeing of suede and glove leathers.

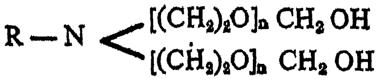
Fatliquors, where the oil is kept in emulsion with the help of cationic emulsifying agents have remarkable stability against acids and solutions of heavy metal salts. Such fatliquors can therefore be applied in combination with chrome and aluminium salts. In the case of chrome leathers, which are retanned with vegetable tanning materials, the cationic fatliquors remain at the outer zones of the leather whereas anionic fatliquors penetrate inside. Also in the finishing, cationic systems such as oils and polymers emulsified/dispersed with the help of cation active bodies are of significant value. Fixing agents for aqueous pigment finishes, which contain cationic fats, work as hardening agents because their charge is opposite to the anionic finishes. At the same time, they also work as softeners and impart to the leather a softer handle.

Highly interesting applications could also be found for amphoteric auxiliaries in the leather manufacture. Auxiliary tanning materials containing in their molecule not only an anionic group but simultaneously a nitrogen atom as well, could be synthesised. These are applied for most divergent purposes. Thus, several pretanning agents for vegetable leathers as well as retanning agents for chrome leather are available on this basis ; as pretanning agents they quicken the tannage and impart a lighter colour to the leather whereas, as retanning agents of chrome leathers, they improve the fullness and capacity for being buffed. Remarkable amphoteric tanning materials with no sulphonic acid groups, but containing an assembly of phenolic groups in the molecule besides an amino group, are used especially for an after-treatment of vegetable tanned leathers in order to improve their fastness to water and sweat as well as their ability to be dyed. In acid medium they are cationic, in neutral and alkaline media anionic. The structure of these tanning materials can be illustrated by the following scheme :



The astringency of these tanning materials increases with increasing pH value, in contrast to the vegetable tanning materials. (Mauthe " Das Leder " 4, 53/1953). The binding on the collagen follows through hydrogen bonds in which the phenolic groups work as proton donors.

Non-ionic surface active auxiliaries are obtained frequently, by combination of ethyleneoxide with hydrophobic substances like higher fatty acids or alcohols. The ether oxygen atoms contained in the hydrophilic part provide the necessary affinity to water. In this case they facilitate the building of hydrogen bonds to the water molecule, acting as electron donors. An accumulation of the ether oxygen atoms in the molecule will be necessary to produce sufficient water-solubility. The hydro-philic part of such auxiliaries is therefore enlarged and the activity of such surface active bodies is determined by the relative proportion of the hydro-philic to the hydrophobic part of the molecule. Non-ionic auxiliaries do not possess any remarkable affinity to collagen ; they are therefore applicable equally well both in acid and in alkaline conditions. By reaction with chrome leather, individual ether-oxygen atoms can also be built in as complexes inside the chrome, which remain however sufficiently unbound to be reactive. Chrome leather treated with hydroxy ethylated products and dried subsequently allows itself to be wetted back easily with water. With vegetable as well as with some replacement tanning materials these hydroxyethylation products give precipitates. Evidently hydrogen bonds are formed between the ether oxygen and the phenolic OH group whenever the latter is largely available Of particular interest are such non-ionic surface active auxiliaries as emulsifying agents for oils, fats and organic solvents. For this purpose they are applied either alone or in combination with organic fatty solvents in order to de-grease pelts as well as chrome leather. When these ethylene oxides are reacted with amines, certain compounds are obtained which have a weak cationic character due to substituted nitrogen atoms :



$$R-N\begin{cases}[(CH_2)_2O]_n\ CH_2OH\\ [(CH_2)_2O]_n\ CH_2OH\end{cases}$$

Because of this they exhibit a weak affinity for anionic dyestuffs without their getting precipitated. In this manner they reduce the affinity of the anionic dyestuffs to make them good for dyeing and act as levelling agents. They can be applied with advantage as levelling agents in the spray dyeing of leather with anionic dyestuffs.

A FEW INDIGENOUS CHEMICALS IN TANNING AND LEATHER INDUSTRY

BY

M. B. DESAI, N. G. MADAN AND D. C. SHAH

(The Kesar Sugar Works Ltd., Bombay)

ABSTRACT

The Chemical Industries of India, are providing today necessary processing materials to many industries including the Tanning and Leather Industry. The Photographic and Fine Chemicals Industry, especially supplies Indian Leather Industry with useful chemicals like hypo, sodium bisulphite, sodium sulphite (anhydrous), potash chrome alum and sodium acetate, of quality conforming to standard specifications. The installed capacity with respect of these chemicals and the scope of their use in the Leather Industry are reviewed in relation to the increased production of leather in the country ; it is concluded that the Indian Chemical Industry is quite vigilant of the growing requirements of the Tanning and Leather Industry.

Introduction

World War II was responsible for the development of quite a good few Chemical Industries in India, due to the failure of imports, and the same proved to be a blessing in disguise, as it gave an impetus to the promotion and growth of indigenous industry. The phenomenal growth of the Tanning Industry itself and its expansion during the last decade provides an example of such a benefit. The policy of the Government of controlling all imports of items that are and that could be easily manufactured in the country, has enabled the manufacture of many chemicals and helped in their healthy growth.

Chemical Industries today are providing necessary processing materials to almost all Industries like Photography, Cinematography, Pharmaceuticals, Canning and Food, Textiles, Rubber, Paper and Pulp, and the Tanning and Leather Industry is no exception. Local production of chemicals like hypo (sod. thiosulphate), sodium bisulphite, potash chrome alum, sodium acetate, sodium sulphite, sodium bichromate and sodium sulphide, myrobalan extracts, syntans and other tanning extracts and dyestuffs used in tanning and leather industries became an urgent necessity, as other countries from where we were importing chemicals prior to World War II, were unable to export these items, firstly because they needed themselves in increased quantity, and also because of obvious transport difficulties during war years. It was during this, and postwar difficult times that the productions of many of the above stated chemicals started, and have today stabilised due to the import restrictions imposed by our Government. Such productions, save the Indian Union valuable foreign exchange and help to provide labour and technicians a steady employment.

The photographic and fine chemical industry is expanding and has attained its targets during The First Five-Year Plan and further expansion of above chemicals during the Second Plan period is going ahead as per the schedules, due to the fillip it received from the consumers as well as from the Government Policy of protection to this indigenous industry from 1946 onwards.

Today the installed capacity of the above chemicals is more than country's requirements, and is meeting the requirement not only of Photographic and Cinematographic Industry but many other industries listed above, including the Tanning and Leather Industry.

In this paper we do not propose to go into the details of all the groups of chemicals listed above, but will restrict to the main-indigenous photographic chemicals used by the Tanning and Leather Industry which are as follows :

Table I

Name of the Chemicals	Installed Capacity	I.S. Specification Number (Tentative) for Technical grade	Percentage Purity
			(Percent)
1. Hypo (Sodium Thiosulphate) ...	1500 (Tons)	246—1950	97 to 101
2. Sodium Bisulphite ...	900	248—1950	55 to 58 SO_2
3. Sodium Sulphite (Anhydrous)	600	247—1950	92 to 94
4. Potash Chrome Alum	120	332—1951	97.5 to 99
5. Sodium Acetate Crystals and Anhydrous ...	As per demands	557—1954	97 to 99

Quality of products

Quality of the indigenous products have considerably improved during the last decade and Indian Standards Specifications have been prepared indicating (Table I) Purity Limits. The indigenous products almost comply with these Standard Specifications and this will inspire the confidence of consumers as the quality of indigenous products is comparable to imported ones.

Leather Industry

Upto the World War II the internal consumption of all type of footwear, chrome tanned hides, vegetable tanned buff and cowhides was low and limited, and there was a tendency to export mainly raw hides to Western Countries but during the last decade, not only the internal consumption has gone up but the exporters are concentrating on sending out semi-finished and finished products to Western countries as could be seen from Table II.

Table II

Figures showing comparative increase in production of Leather and Auxiliaries

Year	Footwear (Western type) (1,000 pairs)	Footwear indigenous type (1,000 pairs)	Chrome tanned Hides (1,000s)	Vegetable tanned buffalo and cowhides (expressed in terms of Cowhides) (1,000s)	Leather Cloth 1,000 yards
1950	2,836.8	1,996.8	495.6	1,514.4	...
1951	3,640.8	2,073.6	879.6	1,704.0	1,918.8
1952	3,367.2	1,806.0	650.4	1,478.4	954.4
1953	3,348.0	2,204.4	700.8	1,298.4	985.2
1954	3,267.6	2,062.8	668.4	1,370.4	1,261.2
1955	3,242.4	2,302.8	676.8	1,635.6	2,623.2
1956	3,620.4	2,911.2	741.6	1,683.6	2,640.0

(Reprinted from page 136, "*Journal of Industry and Trade*" January 1958, Ministry of Commerce and Industry, Government of India, Vol. VIII, No. 1.)

This favourable situation has resulted in gradual increased consumption of sodium bisulphite and hypo in the country. There has also been considerable expansion of the Tanning and Leather Industry on cottage and small scale, and it has today attained the status of a "Major Industry" of our country employing thousands of persons. It will not be out of place to mention the important role played by various Central and State Government Tanning Institutes at Madras, Calcutta, Kanpur and Bombay for imparting sound technical knowledge to our young technicians, in the latest techniques for specialised leather manufacture and also C.S.I.R. institutes like the National Chemical Laboratory at Poona and the Central Leather Research Institute, Madras for the research and development of the chemicals required by the industry.

Uses of Sodium Bisulphite, Hypo, Chrome Alum and Sodium Acetate in Tanning and Leather Industry

Having outlined the general development, let us assess the uses of sodium bisulphite, hypo, chrome alum and sodium acetate in Leather Industry during the processes of (*a*) preparation of skins for tanning and (*b*) tanning the skin.

In the preparation of leather we have to go through each step successively right from raw hide to finished leather. If proper care or attention is not paid to its preceding step, the leather that is obtained in the final stage definitely has its adverse effects. Without going into the details of every step (which we can find in any Std. Text Book), we will see, here the use of certain quality chemicals indigenously manufactured in our country and its effective use in Tanning and Leather Industry.

Sodium Bisulphite is used as, (i) Bleaching Agent (ii) Cleansing Agent and (iii) Disinfectant in soaking.

The first fundamental step in preparation of skins for tanning is soaking. The object of this step is to clean the skin, wool or hair and also to soften and swell the fibres. Due to want of sufficient soaking we find wrinkles and creases. In addition to this the success of depilation and liming depends on the success of properly soaked material. There are two main factors on which success of soaking depends. (*a*) Temperature of soaking. (*b*) Selection of a proper disinfecting agent.

Temperature has a direct effect on the softening and putrefaction. Experts recommend a temperature of 10°C as a limit for safety above which there is a danger of damage especially when stale skins are being handled.

Tanners do not like the use of disinfectants and they have a strong belief, that it has an unhealthy action on goods in soak, but if selected disinfectants are used, they will not stain skins or swell them and control the multiplication of bacteria and their enzymes. Generally (*a*) Organic disinfectants and (*b*) Inorganic disinfectants are commonly used, but Fleming recommends the use of sodium bisulphite. One pound per 100 gallons is the quantity that is recommended. It certainly has a beneficial bleaching, cleaning and disinfectant action on light skins.

Sodium bisulphite is profitably used for the preparation of highly concentrated and difficultly soluble sulphited quebracho extracts, available in two forms :—(*a*) Normal extract containing the high percentage of insolubles (6–10%). (*b*) Sulphited extract with no insoluble matter and a higher percentage of non-tans than usually present. A certain amount of sulphited quebracho extract is used in the light leather manufacture. This form is readily soluble. Even Dr. Lepetit showed in his work that autoclave treatment of quebracho bark with bisulphite of soda results in certain radical chemical changes and the resulting extract differs in many ways from the natural product. Although producing a lighter colour leather, the sulphited extract has a tendency to harden the grain and render the leather somewhat harsher but in conjunction with acid producing tannins, sulphited quebracho extract will produce excellent leather. In India it will be worthwhile to produce sulphited catechin tannins obtainable from the waste liquors of catechu factories using 1 : 1 mixture of sodium sulphite and sodium bisulphite and autoclaving.

Bisulphite as a reducing agent for chrome solutions

The use of sodium bisulphite as a reducing agent for chrome solutions has definitely increased. During the last war when supplies of chrome alum were restricted and only bichromates were available to chrome tanners, use of bichromates and sulphuric acid together with sodium bisulphite as reducing agent became important. The following formula was more or less in vogue :—

Bichromate of soda	28 lbs.
Water	9 gallons.
Sulphuric acid (1.84 Sp.Gr)	18.5 lbs
Sodium bisulphite powder	35 lbs.
Diluted with water	9 gallons

N.B.—*The bisulphite solution to be added with brisk stirring into the solution of bichromate to which sulphuric acid is first added.*

The function of reducing agent is to convert bichromates into the chromium sulphate, the form in which chromium acts as a tanning agent. There are various organic reducing agents used by tanners, such as glucose, molasses, starch, sawdust etc. Organic reducing agents while helping reduction also introduce undesired impurities to the chrome tanning bath, but sodium bisulphite has four distinct advantages over all of them :—

(1) Sodium bisulphite is easy to handle unlike other organic reducing agents as it is available in free flowing powder form.

(2) It gets completely oxidised and leaves no tarry matter behind in the chrome bath as in case of other organic reducing agents.

(3) It makes a clear chrome liquor solution and no offensive fumes are given out, like other reducing agents.

(4) As it is available as a standard quality product no alterations in recipes are necessary during preparation or its use.

Bleaching chamois leather

Sodium bisulphite is also used as a bleaching agent for several types of light leather like chamois leather, where it is used to an extent of 2.5% on the weight of the pelt in conjunction with acetic acid or sodium acetate.

As a deliming agent : In the manufacture of full chrome box sides, it is used as a deliming agent. Deliming with the help of this salt is very rapid which is a distinct advantage.

$$2\,NaHSO_3 + Ca(OH)_2 \longrightarrow Na_2SO_3 + CaSO_3 + 2\,H_2O$$

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*Late Prof. B. M. Das and co-workers studied the effect of addition of a mixture of sodium sulphite and sodium bisulphite in bag tanning with babul bark. For every one maund of dry leather, four maunds of babul bark was used. Very good results were obtained when 0.5% sodium sulphite and sodium bisulphite was added on the weight of the bark.

Along with the deliming there is bleaching action which is very good indeed and tends to give a bright leather. Goods are paddled in sodium bisulphite solution for a period and then washed, scudded and taken over.

Use of hypo, prior to chrome tanning on alumed leather

Alumed leather takes chrome very well, but prior to chrome tanning intermediate drumming is done in hypo. In this connection following patented process by George W. Alder given below deserves mention.

The skins after drenching and washing, are drained and weighed. For every 100 lbs. of them a solution is prepared consisting of 3 lbs. of sulfate of alumina and 6 lbs. of salt in 3 gallons of water, boiled and allowed to cool. The skins are drummed in this solution twenty minutes. Then 10 lbs. of hyposulphite of soda are dissolved in 3 gallons of water and this liquor is poured into the drum and the drumming continued 15 minutes. To finish the first part of the process, a third solution is prepared by dissolving in 3 gallons of water, 2 lbs. of sulphate of alumina and 3 lbs. of salt. This solution is added to the contents of the drum and the drum is run for thirty minutes. Then usual chrome tanning is done." (For further details refer page 81, Principles and Processes of Light Leather Manufacture by Paul I. Smith, 1942 Chemical Publishing Co. Inc. Brooklyn. N.Y.).

Two bath Chrome tanning and an important use of sodium thiosulphate in the manufacture of Glace Kid

Various double bath processes are used in the manufacture of light leather, but the common principle underlined is as follows.

1. Chroming with bichromate and hydrochloric acid or sulphuric acid and afterwards reducing with (*a*) Hypo with hydrochloric acid or sulphuric acid or (*b*) with solution of sodium bisulphite. The tanning is due to the reduction of chromic acid to basic chromium sulphate in leather, the percentage of basicity depending upon the acidity of first and second bath in the case of reduction with hypo, and only on the first bath in the case of bisulphite reduction. The usual quantity of hypo used in second bath is 20% on pelt weight and in case of goat skins, which are thinner than cowhides correspondingly, 20 lbs. of hypo is required for 400 sq. ft. of finished leather.

One bath chrome tanning with chrome alum

Chrome alum $Cr_2(SO_4)_3K_2SO_4 . 24 H_2O$ is obtained by the reduction of solutions obtained by the action of conc. sulphuric acid on potassium dichromate and is largely used in one bath chrome tanning. For each 1000 lbs. pickled pelt to be tanned, 150 lbs. of chrome alum are dissolved in 50 gals. of water at a temperature of about 85° to 95°C. and when the whole of the chrome alum goes into solution, cautiously add a solution prepared by dissolving 11 lbs. of soda ash or 40 lbs. of washing soda crystals in 25 gals. of hot water and make up to total volume of 100 gallons with stirring. When preparing, the solution can be kept for any length of time before use. Box and willow calf and light hides, are always tanned in one bath liquors which produce a firm, solid and yet fully supple leather, with a fine, smooth grain.

(*a*) *Sodium acetate.*—In Chrome tanning the effect of addition of sodium acetate has a strong stripping action. The addition of 1% sodium acetate to tanning liquor gives leather which satisfies boiling test and the tanning action is faster and gives greater chrome fixation.

(*b*) *Neutralization agent* :—Sodium acetate is also a good neutralizing agent penetrating well and giving complete removal of free mineral acid when used at about 2%. It may well be said that some of the sulphate groups are replaced by the acetate groups during neutralization. Its use improves the physical properties of finished leather.

Conclusion

The above review will indicate that the Indian Chemical Industry is quite vigilant of the requirements of raw materials and auxiliary products of tanning and Leather Industry. Further growth and stabilisation of the existing units will not only meet the growing demand of the Tanning and Leather Industry, but will be quite capable of undertaking manufacture of items and auxiliaries not hitherto made in our country. We are also confident that with the incentive and technical advices offered by our various State and Central Governments through their co-operative departments and the Small Scale Industry Services Institutes and with the training and the research facilities available at Government Tanning Institutes, and the Central Leather Research Institute, there will be ample opportunities for the co-ordination and expansion of the Tanning and Leather Industry and the solutions of various technical difficulties and problems facing the industry in the very near future. Already quite a good number of research papers have been published by various technical institutes including the Central Leather Research Institute, and improved processes and techniques have been developed in close co-operation with the industry. Thus the future of the Tanning and Leather Industry is assured.

Chairman's concluding remarks

I would like to make a few observations on the subject of Leather Auxiliaries. Some of the leather auxiliaries are prepared and used in large quantities, for example, sodium sulphide is required by industries like textile, chemical and also leather. The quantity used is fairly large and therefore, it is possible to pool and produce in various grades suitable for the different industries. However, pancreatic bates are used by no other industry except leather. Also the quantity used is small. The usefulness of the symposium lies in the fact that it not only indicates the materials but also helps in selecting and choosing them.

A study of the quantities of the major materials imported during the past six years is interesting : 40% money spent in importing materials for the leather industry was used for importing raw hides, which are in short supply. 20% are spent on tanning machinery, their spare parts, etc. Wattle bark and wattle extract amount to about 7%. Synthetic tanning materials, abrasives, etc., amount to still smaller quantities. So hides and machinery form the two major items. The chemicals required are small in quantity compared with the items mentioned now. Therefore, it would not be practicable to set up industries for these auxiliaries unless we can think of units economic in size. Bringing into existence large units would be uneconomic. Till recently, we did not have an organic chemical industry. Not sufficient attention was paid to this. Some of the basic materials like benzene, cresol, phenol, naphthalene, etc., were not available. With the implementation of the steel projects and coke oven plants, it would be possible to obtain several of these materials. We have already plans for setting up dyestuffs and pharmaceutical industries. Several of the intermediates of these industries will be extremely useful for the manufacture of auxiliaries and anti-oxidants required by industries like rubber industry. Some of these intermediates might be useful in manufacture of certain leather auxiliaries.

We are passing through changing periods and a certain amount of imbalance is inevitable for the time being. We are actually short of several basic materials and these imbalances cannot be avoided due to certain considerations and reasons.

I wish to thank the Russian delegates who have taken so much interest in our deliberations and discussions. We here, should be aware of the advances made in the Russian leather industry. And I hope there will be more collaboration and co-operation between the Indian Leather Industry and its counterpart in Russia.

Dr. S. M. Bose proposed a vote of thanks.

PROCEEDINGS OF THE TECHNICAL SESSION II

15–3–1958—*Afternoon*

Chairman : Shri Sanjoy Sen, National Tannery Co. Ltd., Calcutta.

Recorder : Dr. D. Ramaswamy, Central Leather Research Institute.

Dr. S. K. Barat of the Central Leather Research Institute, introduced the chairman.

After initiation of the Session by the Chairman, the following papers were presented ;

Aluminium tanning salts and their application in processing of leather.	Read by Mr. R. Selvarangan, C.L.R.I.
Syntans as auxiliaries in leather manufacture.	Read by Mr. D. Mukherjee, C.L.R.I.
Synthetic tanning materials and their importance for the industry of vegetable tanned leather in India.	Read by Mr. T. G. Sane, Chika Co. Private Ltd.
Complexes of hexamethylene tetramine and phenols in tanning.	Read by Mr. S. Ranganathan, C.L.R.I
Plea for treatment of dyeing and tanning substances on the same basis as wattle extract and wattle bark.	Read by Mr. P. V. Vittal Rao, A.V. Thomas Co. India Ltd., Madras.

After a break for Tea, the following papers were presented :

The surface charge of chrome tanned leather—effect of organic acids from it.	Read by Dr. S. Ghosh, C.L.R.I.
Chrome retanned leathers—Use of indigenous tanstuffs, Parts I and II.	Summary given by Mr. S. P. Singaram C.L.R.I.
Bagasse reduced basic chrome liquors.	Read by Mr. T. J. Devassy, C.L.R.I.
Glycerol reduced chrome liquors.	A summary of the three papers was presented by Dr. V. S. Padmanabhan, C.L.R.I.
A note on chromatographic separation of organic acids on paper	
Studies in chrome liquors. Part II : Paper chromatographic investigations.	
Neutralisation of chrome leather.	Taken as read.

BAGASSE REDUCED BASIC CHROME LIQUORS

BY

T. J. DEVASSY AND Y. NAYUDAMMA

(*Central Leather Research Institute, Madras*)

ABSTRACT

A study of the optimum conditions for the preparation of basic chrome liquors by reducing acid dichromate with sugarcane bagasse, the chemistry of the chrome liquor so prepared and the practical tanning trials with the same are reported.

Bagasse is crushed sugar-cane refuse after the extraction of its juice for the production of sugar. We have got an unlimited supply of this material in the States of U.P., Bihar, Hyderabad and Mysore. Though it has high potentialities in the production of pulp, at present it is used only as fuel for the production of steam in the boilers. Calculating on the steam producing capacity of this material, bagasse can cost at the most Rs. 30 per ton. An analysis shows the following :

	(Per cent)
Ash	1.139
Moisture	8.7
Sugar	1.37
Extractable material in	
(1) Alcohol	5.00
(2) Petroleum ether ...	0.5

Cellulose, lignin and pentosan are the main constituents of bagasse as reported by many workers. As the material is very cheap and contains a little sugar and fats, it was thought that this may yield a chrome liquor with good masking effect and some special characteristics and hence its study was taken up.

Bagasse was powdered in a Wiley Mill using 20 mesh sieve. For preparation of chrome liquor sodium dichromate and bagasse powder were made into a slurry with water, heated upto boiling (steam may be used) and the acid (1 : 1) added slowly with good stirring. For complete reduction 25% bagasse on the weight of dichromate was enough along with 95% by weight of sulphuric acid. If proper vessels are used, the heat of reaction itself will complete the reaction. Otherwise a little heating will be necessary. The excess of bagasse is removed by straining through a cloth. When 25% of bagasse on dichromate is used, filtration is not difficult as there will be only very little of begasse left. But when larger quantities of bagasse are used as in the case of molasses reduced liquors, filtration becomes a problem. In both qualitative and quantitative studies, the products of reduction are almost same as in molasses reduced liquor and the quantities of products increase with the increase in bagasse used for reduction. As such it can be expected the tanning characteristics also may be similar to those of molasses reduced liquors. Liquors were prepared using different amounts of pith of bagasse, which forms 35% of bagasse. In the case of pith also 25%, on weight of dichromate, was necessary for complete reduction. By the method described above, liquors were prepared using 25%, 50%, 75% and 100% of bagasse on the weight of dichromate. For comparative purposes a sugar reduced liquor was prepared as usual.

With the increasing quantity of bagasse, the pH of the liquor decreases, gradually from 2.9 to 2.8. The pH of sugar reduced liquor is 2.85. On dilution the pH of each of these liquors increases, the change being a little less in liquors prepared using larger proportion of bagasse. There is a little amount of free acid in bagasse reduced liquors which is absent in sugar reduced liquor. In pith reduced liquor also the pH is 2.8 and increases on dilution as in the other cases. The basicity of the bagasse liquors gradually decreases from 34.2 to 32.0 while that of bagasse pith reduced liquor from 34.3 to 33.7 as compared to 34.0 of sugar reduced liquor. A study of change in pH with time showed that it gradually decreases with time till the 3rd week and then it rises a little. But in the case of basicity, it goes on increasing with time. The detailed study on the chemistry of these chrome liquors will be presented elsewhere.

Using the above liquors 6″ × 6″ pelt pieces from the butt portion of a cowhide were tanned at pH 3.0 under the same conditions and finished as chrome upper. Tanning with sugar reduced liquor was done as control. Leather produced by using 25% bagasse liquor compares very well with leathers from sugar reduced liquor. 50% bagasse was next best. By using bagasse pith reduced liquors, very good leathers were obtained, a little better than those by sugar reduced liquor. The liquor prepared using 25% bagasse was used as such for tanning without filtration. As the powder was very fine, no harm was done to the grain but it gave comparatively better leather than that from filtered liquor. In general, these liquors gave leathers as good as those obtained from sugar reduced liquors.

Tannery experiments were done using bagasse reduced liquor for the manufacture of glazed kid and chrome upper leather as usual with control using molasses reduced liquor. In glazed kid, the leather was as good as the control leather, with no additional special characteristics. In the case of chrome upper, it gives comparatively a little tighter grain, fuller shanks, and a very fine break. The leather made from 25% bagasse liquor was better than that having larger amounts of bagasse during preparation.

This liquor has not been tried for other types of leathers. It must be said that a little adjustment in the initial pH etc., will give a leather better than obtained with molasses reduced liquors. This liquor will be greatly useful in the preparation of leathers with tight grain and fine break. The two disadvantages are powdering of bagasse and filtration after preparation. But we are having very big tanneries using as reducing agent saw dust, which has this disadvantage. Its availability, cheapness and the good characteristics of leather produced are in its favour to attract any enterprising tanner for using it.

DISCUSSION

Mr. S. R. Das (Indian Leather Technologists' Association, Calcutta): Has preparation of bagasse-reduced chrome-liquor been tried on large scale ? If so, what is the cost ? What is the cost of transport of bagasse ? Would this process help the tanner either in realising a higher price for the product or in lowering the cost of production ?

Mr. Devassy: Glazed kid processed this way is as good as chrome upper leather, while chrome upper leather produced was firmer and had a fine grain. The cost has not been worked out.

Mr. R. Selvarangan (C.L.R.I.): Saw dust is similar to bagasse and so could be used in the place of former for reduction.

GLYCEROL-REDUCED CHROME LIQUORS*

BY

T. J. DEVASSY, V. S. PADMANABHAN AND B. N. PAL

(*Central Leather Research Institute, Madras*)

ABSTRACT

Glycerol reduced chrome liquors have been prepared at the boil and with heat of reaction alone. The qualitative and quantitative investigations carried out with these are described.

A study of glycerol reduced chrome liquors was undertaken, as part of a programme of investigating the chemistry of one bath chrome liquors. It was expected that the simple nature of the reducing agent would lead to conclusive studies—studies which would throw light in elucidating the chemistry of glucose and sucrose reduced liquors. Glycerol reduced liquors do not appear to have been studied much. (There is, however, a reference to formation of glyceric and tartronic acids as oxidation products)[1]

Experimental

The liquors were in all cases, prepared by addition of glycerol solution to mixture of dichromate and sulphuric acid, the details of preparation being the same as used by Theis *et al*[2], the reaction system also was essentially the same—a three-necked flask, an efficient condensing system followed by an absorption train. The main changes effected were, absence of a stirrer, dispensing with the suspension of $BaCO_3$ for trapping acid vapours escaping condensation and using when necessary an absorption flask containing a reagent suitable for detection or fixing the aldehydic products. The quantities of potassium dichromate and sulphuric acid taken were in the same proportion as employed by Theis *et al* (loc.cit) and in an earlier work[3,4] : actually 200 ml. of the liquor was prepared in many instances. Stoichiometric and 50% excess, 100% excess, 150% excess and 200% excess over the stoichiometric, quantities of glycerol were employed.

Two series of liquors were prepared—one, utilising the heat of reaction itself and the other at the boil. External heat was applied in the first case after complete addition of glycerol solution, in the second case external heating was discontinued after bringing the solution to boil, being resumed only after addition of glycerol solution was completed. Time of addition was 15 mins. and total time of preparation 2 hrs. Before analysis, the liquors were made up to 250 ml. if 100 ml. of the liquor was prepared and to 500 ml. if 200 ml. A stream of nitrogen was utilised to drive CO_2 and the aldehydic products into the absorption train.

Carbon dioxide, steam volatile acids, formic acid and oxalic acid were estimated by methods used in earlier studies[4]. For glyoxalic acid the method used by Theis *et al* (loc.cit) was followed.

Results and discussion

Aldehydic products : Preliminary experiments raised the doubt whether aldehydes were formed in appreciable quantities. So the gaseous products coming out of the condensing system, in the preparation of liquors with different proportions of glycerine were tested in each case with fuchsin reagent. It was found that aldehyde formation was significant only with 100% excess of glycerol. This was also confirmed by a pronounced yellow colouration of the alkali used for absorbing CO_2. For fixing the aldehydic products, a 2.5% solution of 2 : 4 dinitro phenyl hydrazine in 30% perchloric acid was

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* This work was carried out in a research scheme financed by the Indian Council of Agricultural Research.

found more suitable. A small quantity of the hydrazone precipitate was obtained. Determination of m.p. could not help in fixing the identity of the compound as no sharp melting point was obtained. Chromatographic investigations utilising a solution of the precipitate in ethyl acetate and using a mixture of n-Hexane and methyl alcohol as the solvent were not more useful for there was no movement of the compound spotted. It might be concluded, however, that the aldehyde formed might be a dialdehyde (possibly glyoxal), as dialdehydes were not resolvable with the solvent system tried.[5] At any rate, the aldehydes would appear to be found in very small quantities only, accounting for not more than 1% of glycerol put in and that too with higher percentages of glycerol only.

The steam volatile and non-volatile products of oxidation : In detection of these, spot test and chromatographic techniques were utilised. The relevant results have been discussed in earlier communications.[3] The products of oxidation of glycerol formed in appreciable quantities would appear from these, to be : carbon dioxide, formic acid, acetic acid, oxalic acid and glyoxalic acid ; small amounts of lactic and glycollic acids also are formed. Direct evidence for acetic and glyoxalic acids could not be had and their presence has been inferred from quantitative results only.

Quantitative results : Carbon dioxide, total steam volatile acids, formic acid, oxalic acid and glyoxalic acid have been estimated directly and the results for the two series of liquors prepared are given in Tables I and II.

The mode of preparation of the liquors has a great bearing on the proportions of the various oxidation products formed. Carbon dioxide which is the final product of oxidation corresponding to complete oxidation is formed in greater quantities at the boil ; this is only to be expected as at the boil, conditions would be more favourable for complete oxidation. The amount of volatile acids formed is greater in the series of liquors prepared using heat of reaction, than in those prepared at the boil. When the conditions of experiment are less favourable for complete oxidation, naturally products corresponding to lesser degree of oxidation are formed. In the first series of liquors, the amount of CO_2 formed tends towards a constant value, with increasing percentage of glycerol, whereas in the second, the actual amount of CO_2 formed decreases with increasing glycerol content. Glyoxalic acid has been determined only in one series as it was felt that the method of estimation needed improvement. As far as the results obtained go glyoxalic also is formed in decreasing amounts with increasing proportion of glycerol. A comprehensive consideration of the results is not possible because more accurate data regarding formation of glyoxalic acid are wanted and also because, a suitable method for estimating the excess glycerol has got to be developed. However, the significant fact is that more of the masking products are formed when the liquors are made at the laboratory temperature ; the nil value for oxalic acid in the liquors prepared at the boil is another noteworthy feature. However, as has been shown earlier, the amount of acid formed is only too small to be identified by the usual quantitative method ; it is actually seen in chromatograms. It is expected that further work would provide fuller information.

ACKNOWLEDGEMENT

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GLYCEROL REDUCED LIQUORS (40 gms. DICHROMATE)

TABLE I

(During liquor preparation, heating done only after addition of glycerol)

Glycerol used	Amt. of CO_2 in gms.	Percentage of glycerol converted	Volatile acid (Acetic acid)		Formic acid		Oxalic acid		Glyoxalic Acid	
			Amt. (gms.).	Percentage of glycerol converted	Amt. (gms.).	Percentage of glycerol converted	Amt. (gms.).	Percentage of glycerol converted	Amt. (gms.).	Percentage of glycerol converted
Stoichiometric	3.58	43.3	1.34	23.4	1.00	11.6	0.39	4.7	1.05	15.1
50 per cent excess	3.76	34.0	3.15	41.5	1.62	13.8	0.42	3.7	1.22	12.9
100 per cent excess	3.76	23.3	3.68	33.0	1.86	10.8	0.55	3.3	0.96	7.1
150 per cent excess	3.57	18.0	5.60	43.1	2.06	10.4	0.76	4.0	0.64	4.0
200 per cent excess	3.76	17.0	5.66	36.7	1.96	8.6	0.94	4.2	0.28	1.5

TABLE II

Addition OF GLYCEROL DONE AT BOIL

Glycerol used	CO. 2		Volatile acid		Formic acid		Oxalic acid	
	Amt. (gms.)	Percentage of glycerol converted	Amt. (gms.)	Percentage of glycerol converted	Amt. (gms.)	Percentage of glycerol converted	Amt. (gms.)	Percentage of glycerol converted
50 per cent excess	5.32	47.7	1.74	22.9	0.67	5.8	Nil in all cases	
100 per cent excess	5.10	34.3	1.86	18.4	0.72	4.6	Do.	
150 per cent excess	4.20	22.0	3.4	27.0	0.75	3.9	Do.	
200 per cent excess	4.07	18.2	3.26	21.4	0.8	3.5	Do.	

A NOTE ON 'CHROMATOGRAPHIC SEPARATION OF ORGANIC ACIDS ON PAPER'*

V. S. PADMANABHAN
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ABSTRACT

The role played by correct adjustment of pH values of the test and indicator solutions, in proper resolution of fatty acid components is pointed out.

In investigation of chrome liquors prepared with reducing agents like glycerol, glucose and sucrose, need was felt for a suitable technique for characterising the various organic acids formed. It was proposed to apply paper chromatography as the latter has come to be a well-established technique for analysis of organic acids. In the preliminary work with solutions of known acids, it was found that these solutions used as such did not give successful chromatograms while the unknown solutions did. Since the pH of the latter had been adjusted to be on the acid side, it was thought this difference in pH was responsible for this. The exact significance of the pH of the solution to be analysed, in obtaining good chromatograms does not appear to have been realised. So it was thought necessary to investigate this aspect. The adjustment of the pH of the indicator solution used for developing finds mention in literature[1]; however this also was included.

Approximately N/10 solutions of ammonium and sodium salts of formic and acetic acids (and mixtures of the same) were prepared. These were adjusted to pH values of 6.0, 5.5, 5.0, 4.5, 4.0, 3.5 and 3.0 and then spotted. The ammoniacal alcohol used as the solvent was the same as employed by Long, Quayle and Stedman.[2] After irrigation for 6–8 hrs. the papers were removed, dried and then developed with the indicator solution. 0·04% alcoholic solutions of bromo cresol green and bromo cresol purple were used individually. The indicator solutions also were adjusted to various pH levels *i.e.*, 8.5, 8.0, 7.0, 6.5, 6.0 and 5.5. (Whatman Filter paper No. 1 was used throughout).

The spots due to the acidic components could not be seen if the pH of the solution was more than 4.5 and if the pH of the indicator solution was less than 7.0. The optimum values were 4.0 for the solution to be analysed and 8.0 for the indicator solution. pH values lower than 4.0 tended to make the spots diffuse. Of the two indicators bromocresol green was found to be better. In any case, the spots had to be outlined in pencil immediately after developing, as the colour of acid spots faded with time. The above procedure was used in the investigation of chrome liquors.

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DISCUSSION

Mr. V. R. Kishore (C.L.R.I.) : Could paper chromatography be applied for separating sulphated oils with higher fatty acids content ?

Dr. V. S. Padmanabhan : Since the question was beyond the purview of the paper presented, I would be glad to investigate if necessary.

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STUDIES IN CHROME LIQUORS : PART II
PAPER CHROMATOGRAPHIC INVESTIGATIONS*

BY

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ABSTRACT

In applying paper chromatography to investigation of chrome liquors, elimination of cationic interference was necessary. The results obtained after such elimination are considered in the light of information obtained by other means.

In the previous part[1], reference was made to the limited information by application of paper chromatographic technique in investigation of chrome liquors. The main difficulty in correct interpretation of the chromatograms was the interference by the cations (Na^+ and K^+) present in the solutions spotted, these cations revealing themselves on developing as blue spots of large area, which in all cases overlapped the yellow spots produced by the acid components. Another difficulty was the closeness of R_f values of some of the components. It was felt that the replacement of Na^+ and K^+ ions by NH_4^+ ion would eliminate this interference. The results obtained by doing this in the case of glycerol reduced liquors are reported in the present paper.

Chrome liquors were prepared using ammonium dichromate instead of sodium or potassium dichromate ; for preparing the Cr-free solution to be used for spotting, ammonium hydroxide was used instead of sodium hydroxide to precipitate the chromium. The solutions thus obtained were analysed through unidimensional paper chromatography, using ammoniacal alcohol and butanol-acetic acid-water mixture. The chromatograms were developed with bromo cresol green on bromo cresol purple. The studies were primarily with glycerol-reduced liquors with some extension to glucose and sucrose reduced liquors also.

Cationic interference was found to be completely absent in the chromatograms obtained, the organic acids revealing themselves as yellow spots against the blue background, the blue spots being totally absent. The spots due to the acids could be seen in their correct form and number. The pattern of the chromatograms obtained with the liquors using different percentages of glycerol was the same in all cases (the colour intensity alone varying) and was as follows : a yellow streak starting from a little above the starting line, then a strongly yellow spot of comparatively large width and lastly a half moon-like spot. The streak and the strongly yellow spot were not clearly seen when Na^+ and K^+ were present.

In fixing the identity of the components producing the spots, the absolute R_f values were not utilised as these were liable to vary with changes in experimental conditions, like temperature, time of irrigation, paper texture and so on. So for identification along side the unknown solutions were spotted in the same paper, solutions of known components—oxalic, glycollic, lactic, formic and acetic acids, the acids indicated by spot tests (vide Part I)[1]. By comparison of the spots seen after irrigation and developing, the presence or absence of any particular component was inferred. The pattern of the chromatogram got with known components was as follows ; a streak due to oxalic acid, the spot due to glycollic acid occurring next, acetic and formic acids to-

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* This work was carried out in a research scheme, financed by the Indian Council of Agricultural Research.

gether giving the next spot and lastly a little higher a spot due to lactic acid. On comparison of the chromatogram of the solution under investigation with these known spots, it was seen that the half-moon like spot corresponded to acetic and formic acids ; however, with the solvent used—alcoholic ammonia, further resolution into the two acids was not possible a fact confirmed by experiments with known mixtures of the two acids and also in literature. Since the position of the lactic acid spot also was quite close to this, no unequivocal decision regarding its presence was possible in this set of experiments. The streak confirmed the presence of oxalic acid—an inference not possible when the cations $K^+$and Na^+were present. No spot corresponding to glycollic acid could be seen. The large bright yellow spot in the unknown chromatogram was thus found to correspond to none of the known components spotted.

In the next set of experiments, n-butanol-acetic-acid-water mixture (4 : 1: 1) was used. With this solvent system, acetic and formic acids cannot be identified ; however dicarboxylic acids and lactic and glycollic acids were resolvable. The pattern of chromatograms given by Cr-free solutions from liquors was : a large bright yellow spot, surmounted by an elongated spot. The latter could be readily identified by comparison as corresponding to oxalic acid while the former could not be checked in as before with any of the known acids tried. Lactic and glycollic acids were indicated to be absent.

A propos the unidentified spot, it may be mentioned that glyoxalic acid has been reported to occur in significant amounts in glucose-reduced chrome liquors.[2] In glycerol reduced liquors, this acid has been found to be present in comparatively large amounts.[3] Further a spot in the same position has been found in chromatograms obtained in analysis of chrome liquors prepared by reduction with bagasse and coconut pith.[4] Putting all the observations together it would seem reasonable to conclude that the spot corresponds to glyoxalic acid. A direct identification has been not possible, because of non-availability of glyoxalic acid samples.

Coming now to the quantitative significance of these results, it may be stated, that though oxalic acid has revealed itself in these chromatograms, zero value was obtained in the quantitative experiments based on the usual permanganometric method and that glycollic and lactic acids though indicated by spot tests, are not seen in the chromatograms. So of the various acidic oxidation products of glycerol identified, only acetic, formic and glyoxalic acids (to some extent oxalic acid also) are formed in significant amounts ; the rest would seem to be present in very small quantities only. While the present study has been mainly with glycerol reduced liquors, preliminary experiments would appear to indicate similar results with glucose reduced liquors also.

Experimental

The preparation of the liquors was done at the boil under the same conditions as mentioned in the previous paper[1], substituting ammonium dichromate for potassium dichromate. The proportions of glycerol used were 50% excess, 100% excess and 150% excess over the theoretical amount needed for complete reduction. No absorption train was used ; however, products other than carbon dioxide and aldehydic products were not allowed to escape.

The solutions for chromatographic studies were obtained by precipitating Cr as the hydroxide using conc. NH_3 in excess. The chromium hydroxide was filtered off and the total volume of the solution adjusted to 50 ml. Before spotting the solutions were brought to pH 4.0. Solutions of the known components were prepared by dissolving the respective acids in water so as to give a 0.5%

solution. Five of each of the solutions were spotted at a time. Whatman No. 1 filter paper was used. The apparatus used for 12″ × 12″ paper was the one described by Mathew and Das[5], for 18″ × 12″ paper, a big bell-jar, fixed inverted in a stand and provided with a lid was used. The composition of ammoniacal alcohol solvent was as given by Long, Quayle and Stedman.[6] n-Butanol-acetic acid-water system (4 : 1 : 1) was prepared by simply shaking the components together. Irrigation was half an hour after spotting. Developing was, after drying overnight, with a 0.04% alcoholic solution of bromocresol green, adjusted to pH of 8.0 with NaOH solution.

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NEUTRALISATION OF CHROME LEATHER

BY

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ABSTRACT

The behaviour of certain complex active organic salts as neutralising agents for chrome leather has been investigated. The alteration they bring about in the nature and charge of the complex and the consequent changes in the dyeing and fat-liquoring properties of the leather have been studied. The specific advantages such as fulness and better feel in the leather obtained by the use of these salts have been pointed out.

The importance of the process of neutralisation of chrome tanned leather has been realised for quite a long time but very few attempts have been made to explain the mechanism of neutralisation in the light of the various factors that are involved in the process.

Much work has been done in the study of neutralising agents like bicarbonates of sodium and ammonium and borax ; though it has been known that the feel and the quality of the leather could be improved by certain complex active salts, a correlation between the chemical nature of the chrome complex and the physical characteristics of the leather has not been attempted in the past.

Hence work has been carried out in this Institute using salts of certain organic acids as neutralising agents and their effect on the chrome complex and the physical characteristics of the leather produced studied. The salts investigated were oxalate, phthalate, acetate and adipate.

The neutralising action of any particular organic salt depends upon (i) ionisation constant of the organic acid and (ii) its buffering capacity. Though the amount of the neutralising agent is high as compared to customary neutralising agents, the risk of overneutralisation is little as these agents exert their neutralising action through their buffering capacity. Also, it has been observed that the protein bound acid is removed at pH 4.5 ; it therefore presents a method in which neutralisation can be carried along with tanning by completing the tanning at pH 4.5. The precipitation of chromium as chromium hydroxide is avoided by these salts at pH 4.5, because of their complex forming tendency.

The study of the basicity of the complexes and the basicity of the leather shows that they do not alter the basicity even at higher pH values. They do not introduce additional—OH groups into the chrome complex. But when they are used in higher concentrations, they tend to displace the complexly held groups and strip the chrome as well. But it has been observed that the concentration necessary to obtain a pH of 4.5 is not high. The additional advantage of neutralising the protein bound acid, without overloading the complex with too much of groups which is very much desired, is achieved by the use of these salts.

A study on the effect on sulfato acidity indicates that the anions of the neutralising agents penetrate into the chrome complex depending upon the nature and concentration of the anion, forming complexes of different charges and stability and tanning properties. Hydrothermal stability is not influenced to any great extent by the sulfato acidity. When these salts are used in reasonable amounts they impart certain desirable characteristics to the leather.

A study of the hydrothermal stability characteristics reveals that the T_s is related to chrome content, basicity and the nature of the complex. The T_s is maximum at pH 4.5—5.0 and at higher pH values, it is considered likely that non-ionic and anionic complexes might be formed which have lower tanning potency and hence reduce the thermal stability.

The dyeing and fat liquoring characteristics of the neutralised leathers have been investigated. With the use of these complex active salts the affinity for anionic dyestuffs is reduced and affinity for cationic dyestuffs is increased, thereby helping to achieve more level and uniform shades. The reduction of the highly positive surface charge of chrome leather is particularly useful in retanning of chrome leather.

The crackiness, the usual difficulty encountered in chrome retannage, is due to the great affinity of vegetable tannins for chrome leather. This affinity is considerably reduced and the grain crackiness is eliminated to a great extent by the use of these complex active salts.

The fat liquoring properties are considerably influenced by the protein bound acidity and basicity and the nature of the chrome complex formed during neutralisation. It has been observed in certain cases, that the amount of the fat liquor needed to produce a desired effect is also less.

The study clearly indicates that the complex active salts when used in controlled mounts produce certain desirable characteristics in the finished leather which is not generally achieved by the customary neutralising agents.

ALUMINIUM TANNING SALTS AND THEIR APPLICATION IN PROCESSING OF LEATHER

BY

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ABSTRACT

The paper gives a brief account of the history of alum tawing and its drawbacks. It reviews the work done in alum tanning and describes the preparation of various basic aluminium salts—alone and in combination—and their uses in combination with mineral tanning agents like chrome, iron, zirconium tanning salts and organic tanning agents like tannin, water soluble resins and formaldehyde. The aluminium tanning salt can be used advantageously in the manufacture of leather intended for grain and flesh finish, for sports and industrial purposes. It can be used in the manufacture of uppers, sole leather, upholstery and fancy leathers. It can also be used as a mordant in dyeing.

The use of alum and salt in preserving the hides dates back to the Bronze Age. The flesh side of the hides was rubbed with salt and alum, stored in a cool place for a few days and then stretched and pulled. This method came down to the Romans who perfected it in producing their fine leather known as " Aluta." In the Middle Ages, the Moors in Spain produced a very soft leather tanned by means of alum and salt.[1,2,3]

The process of alum tanning known as " tawing " wherein a mixture of alum, egg-yolk, oil, flour and common salt used for tanning was found to be unsatisfactory for certain reasons. The alum tanned leather turns yellow on ageing, becomes hard on drying, detans on washing and sweats in humid atmosphere.

Much interest has not been shown in the development of alum tanning, as chrome tanning became very prominent, thanks to the work of Schultz[4] who contradicted the finding of Knapp[5]. However numerous patents and a few papers on the use of aluminium salts in straight alum tannage,[6,12] in combination with carboxylic and hydroxy carboxylic acids and their salts[13,23] formaldehyde[24,25] vegetable[26,29] chrome[30,31] syntan[32] water soluble resins,[33] silicate[34,36] and pyrophosphate are found in literature but they are not yet industrially adopted due to the difficulties in the process and insufficient knowledge on the chemistry of complex aluminium salts and their tanning action.

The German products Blancoral A and B (Basic aluminium chloride 45–50% and 70% respectively) and the American products Telaon (basic aluminium acetate)[37] and basic aluminium sulphate available in the foreign markets find little use. The basic aluminium sulphate marketed contains considerable amount of insolubles and it is not stabilized well to obtain a clear solution of basic aluminium sulphate at pH 4.2 to 4.5 at which the fixation of aluminium readily takes place. Blancoral A and B are used in Germany to retan chrome leather ; aluminium acetate finds use in retanning of vegetable tanned leather in U.S.A. Blancoral A and B are hygroscopic and yellow in colour and they have not yet become popular. Hence, the preparation of alum and combination tanning extracts and their uses in tanning should be of theoretical and practical importance.

Aluminium sulphate or chloride solution at high concentration can be made highly basic by the addition of sodium carbonate. The basic aluminium chloride can be diluted without hydrolysis for use in tanning. But the chloride is inferior to the sulphate as a tanning agent. Highly basic aluminium sulphate which is not stabilized by the addition of masking salt cannot be used as such in tanning and on dilution, hydrolyses. This basic solution can be diluted by adding sodium sulphate solution. But, however, the presence of considerable amount of salt in tanning solution retards the fixation of aluminium. Hence a number of masking salts were tried for stabilising aluminium sulphate solution at moderate dilution and citrate was found to be a good masking salt. But addition of masking salt beyond an optimum amount for each salt will decrease the fixation of aluminium. Highly basic aluminium sulphate[38] stabilized with citrate was prepared for use in tanning. It can be used, like chrome, in one bath tanning, with or without addition of salt in the tanning bath. Besides basic aluminium sulphate, other aluminium tanning extracts like basic aluminium chloride[39], basic aluminium chromium sulphate[40] and aluminium vegetable tannin extracts[41] also have been prepared.

The basic aluminium sulphate does not impart any colour to the pelt in tanning and hence it is very suitable where whiteness of the leather is an important factor. Hence it can be advantageously used in white tannage *e.g.*, white tanning of snake skins,[42] white buck leathers, white sheep linings, hockey ball leather, white glove leather, other sports goods leathers etc. The Calgon pickling and formaldehyde before or after tanning assists the aluminium white tanning.

The addition of aluminium salts to chrome liquor or chrome tanning before or after tanning with aluminium salts improves the quality of the chrome leather produced. Hence wherever chrome is used, aluminium salt can also find a place and basic aluminium sulphate can be used in the manufacture of glazed kid, chrome uppers, upholstery, picking band etc.

The quality of leather produced by zirconium, iron, silicate and water soluble resins was found to improve considerably when these agents were used in combination with basic aluminium sulphate tanning salts.

Basic aluminium sulphate can be used in combination with vegetable tanning. Semi-alum leather can be used as upholstery leather[43], upper, sole leather, harness leather, belting leather, clothing leather, stuffed leather, picking bands, sambhur, suedes, bookbinding leather etc. Alum retan leather can be used in the manufacture of picking band[44] roller skin, belting leather etc.

The aluminium retanned leathers are equal and in many cases, superior to the chrome tanned leathers in strength and resistance to heat and acids.[28 29] Semi-alum tanned leather has a tendency to crack and soften. Vegetable tanned leather increases in thickness and air permeability on alum retanning with appreciable decrease in water absorption. The leather may become more water repellant when the semi-alum leather is fatliquored, due to the formation of aluminium stearate complexes of water repellant nature. Hence alum retanning can be advantageously used in the manufacture of upholstery leather, uppers, clothing leather, insoles, kavalai hides, splits etc. The semi-alum tanned leather takes more of stuffing material on impregnation due to the increase in the void interfibrillary space on alum retanning and higher hydrothermal stability of the leather. Basic aluminium chloride can be used in the place of sulphate of aluminium followed by a treatment with sodium sulphate solution in certain cases.

The aluminium-chrome combination extract was used advantageously in the manufacture of glace kid by a single bath process, uppers, glove leather and upholstery leather.

The aluminium-vegetable extract produces a soft type of leather. It can be used in the manufacture of clothing leather, suedes and hydraulic leathers. Aluminium tanning salts can be used to finish sheep skins as clothing leather, suedes, linings, fur skin, rollers skin, diaphragm leathers, hat felt, book-binding leather etc.; goat skin as glace kid, chamois, bookbinding, suedes, linings, shrunken grain leather etc.; reptile skins as white tanned skins ; cow hides as uppers, sambhur, foot-ball leather, white buck, sport goods leather, lace leather etc.; buff hides as sole leather, insole leather, impregnated leather, belting leather, cycle seat leather, hydraulic leather, kavalai leathers, picking band, lace leather etc. The aluminium tanning salts can also be used in other applications. The basic salts are used to fix the dyes and intensify and brighten the shade in leather and textile dyeing.

Thus aluminium tanning salt can be used advantageously in manufacturing leather intended for grain and flesh finish, and for sports and industrial purposes. It can be used in the manufacture of uppers and sole leather, for upholstery and fancy leathers. It can also be used as a mordant in dyeing.

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Discussion

Chairman : I would like to know whether the conclusion regarding improvement of the quality of leather was from chemical consideration, physical consideration or the consumers' point of view.

Mr. R. Selvarangan : The conclusion is from the consumers' point of view. While the ordinary chrome tannage produces often papery leather, retanning with aluminium salts improves the quality, making the leather fuller, softer and of greater substance, thus fetching a higher price. Glazed kid could be produced by single bath chrome tanning and aluminium tanning.

Chairman : What has been your experience in regard to vegetable tanned leather ? What are the difficulties in fatliquoring, when aluminium is used?

Mr. R. Selvarangan : In straight alum tannage there is difficulty if anionic fat liquors are used. But with vegetable pretanned and aluminium retanned leather, the difficulty is not encountered. Aluminium retannage assists fatliquor uptake. The fatliquor employed was composed of 2 parts of free oil (Castor Oil) and one part of sulphonated oil, sulphated pongam oil, Borax, soap, etc. While vegetable and aluminium tanned leathers have T_s round about 80°C, aluminium retanned and chrome retanned leathers have T_s of 100°C. Chrome tanned leather becomes flat in shanks, while aluminium retanned leather is fuller.

Mr. Nazir Hussain (Perambur Chrome Tannery) : Could aluminium tannage be applied to chrome suede leathers ?

Mr. R. Selvarangan : Aluminium tannage produces a good nap while vegetable aluminium combination tannage gives a better nap. Water-proof leather is obtained. I prefer cowhides instead of goat and sheep skins as the latter are costlier. The thickness would be considerably increased ; the grain layer could be used for clothing and the flesh for insole. Lacquer spoils the feel and so lacquer emulsion would be recommended for clothing leather only.

Dr. Y. Nayudamma: For what could aluminium tannage be not used ?

Mr. R. Selvarangan: With straight aluminium sulphate tannage, sometimes a hard leather is obtained. This could be set right by use of formaldehyde and calgon with pH greater than 4.0. However this modification could not be followed in the presence of hot water.

Mr. S. C. Das (Indian Leather Technologists' Association, Calcutta): Could the author recommend this process for the benefit of the Indian tanners as the hide production was limited ? If so, what would be the price that the leather would fetch ?

Mr. R. Selvarangan: The leather has got to be first vegetable tanned and retanned with aluminium. Otherwise, precipitation would occur at higher temperatures. In certain cases, however, aluminium tannage followed by vegetable tannage could be done as in the case of skivers and diaphragm leathers.

SYNTANS AS AUXILIARIES IN LEATHER MANUFACTURE

BY

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ABSTRACT

Preparation of two types of syntan, *viz.*, Neradol and Novolac is briefly described. The use of these materials as bleaching, pretanning and retanning agents as well as for replacing of the vegetable tanning materials is elaborately brought out with specific examples of work done in this regard at this institute with the materials prepared here.

Synthetic tanning materials are high molecular organic compounds (not of natural origin) or mixtures of such compounds capable of converting animal skins into leathers. Stiasny differentiated "synthetic tannins," *i.e.*, which are made synthetically and having the same constitution and the "artificial tannins," *i.e.*, those showing only analogies and resemblances in constitution and behaviour to those of vegetable tannins.

The synthetic tanning materials of the Neradol D type, are generally prepared by first sulphonating an aromatic compound *viz.*, cresols, phenols and naphthalene with concentrated sulphuric acid at an elevated temperature. By doing so, hydrophilic group $-SO_3H$ is introduced into the benzene ring and the product becomes soluble in water. The simple sulphonic acids have no tanning properties. So, these are then condensed with an aldehyde, mainly with formaldehyde, at comparatively lower temperature to impart the tanning potency.

The product thus obtained is highly acid and in order to avoid the harmful effects of swelling the protein, the syntan should be partially neutralised to remove excess of free sulphuric acid. Sulphonic acid combines with the basic groups of the collagen. The tanning power of this type of syntan is due to $-SO_3H$ groups combining with the amino group of the collagen to form a salt link.

Formaldehyde condensation products of cresols or phenols sulphonated subsequently yield plumper leather than the products obtained from cresol or phenol sulphonic acid which is subsequently condensed with formaldehyde. These syntans possess better filling properties and consequently produce better leathers. Novolac resins are prepared by the condensation of phenol with formaldehyde using an acid catalyst. Provided that the ratio of phenol to formaldehyde exceeds 1, the resinous products formed under the influence of an acid catalyst are permanently fusible and do not harden upon heating to an insoluble and infusible mass. The usual molar ratios of phenol to formaldehyde varies from 1 : 0.8 to 1 : 1. Under the usual manufacturing conditions, the products obtained in the presence of acid catalyst differ appreciably from those obtained when alkaline catalysts are used. Novolac syntans are generally prepared by first condensing the phenol with formaldehyde using an acid as a catalyst, and after removing the water formed during reaction, the dry resin is sulphonated with concentrated sulphuric acid.

Most important factors that affect the tanning properties of the syntans of the Novolac type are the degree of condensation and the degree of sulphonation. It has been actually found by repeated experiments that the degree of condensation and hence the particle size of theNovolac syntans are responsible for better tanning effects. But if the particle size is too big, it would be very difficult to sulphonate and to make it penetrate into the pelt.

The synthetic tanning materials are readily distinguished by their anionic character. Whilst some are pronouncedly strong acids, in contrast, others of a different character having number of phenolic hydroxy groups, are found to be similar to the weak acids present in vegetable tanning materials. It has been found that Novolac type syntans, though producing a full and tight leather, impart reddish brown to red colour on the finished leather. Poor colour or deterioration of colour in leathers may be due to formation of quinone-like bodies by oxidation. The colouration is due to the oxidation of the aromatic substances during the sulphonation processes if high temperatures are used. The presence of the number of phenolic OH groups in syntan is responsible for this dark colouration, though these phenolic hydroxyl groups are equally responsible for its tanning action. The removal of these OH groups removes the tanning potency of the syntan. In order to minimise the red colouration, these OH groups should be properly protected from oxidation without destroying them. One of the ways of reducing the formation of these chromogenic groups is sulphitation. The process of sulphitation checks considerably the formation of these red colours but at the same time reduces the affinity of the syntan towards the collagen. Another way of reducing the formation of the red colour is acylation. The powerful agents for acylation of phenolic compounds are acetyl chloride or acetic anhydride in pyridine medium.

Thus it is evident that in Neradol D type syntans the SO_3H groups are responsible for the tanning activities, whereas the SO_3H in Novolac syntan is important only as a solubilising agent. The tanning potency of Novolac syntans is due to number of phenolic OH groups.

As has been mentioned earlier Neradols cannot be used alone for tanning, while Novolacs can replace vegetable tanning materials to a great extent. Another class of synthetic tanning materials being used in leather manufacture, are amphoteric tannins. These syntans whose solubility depends not on sulpho groups but on the hydrophilic properties of quaternary ammonium salts, are obtained by a mixed condensation of monophenols, aldehydes and aromatic amines in an organic solvent.

Some of the most important uses of Neradols are for bleaching and pretanning of vegetable tanned leathers. It has been found out that Neradol type syntans when used for bleaching, strip out vegetable tannin from the leather to some extent. The bleaching of vegetable tanned leather was formerly done by brushing dilute solutions of oxalic acid. Similarly, the colour of the vegetable tanned leather can also be lightened by dilute solutions of other acids like sulphuric acid. The acid strips out the topmost layer of vegetable tannin which has been oxidised during the tannage. But this is temporary because after some time the loose vegetable tannin will ooze out and fix on the top layer, which will again oxidise in course of time. However, if the leather is treated with dilute solutions of auxiliary syntan, it not only strips out the vegetable tannin from the top but gets itself fixed on the leather and thereby retards the further oxidation. As the colour of the syntan is very pale, the colour of the leather becomes light.

In pretanning with the auxiliary type syntan, the sulphonic acid groups attach themselves to groups in the protein molecules that would otherwise fix tannins. The slower moving tannins being not fixed by groups already occupied by syntan, are then able to diffuse further into the skin thereby increasing the rate of diffusion of the tannins.

Semi-chrome leathers have been prepared at the Central Leather Research Institute from E.I. Kips by first stripping with the condensed cresol-sulphonic acid at pH 1.8 and then after thorough washing, retanning with basic chrome sulphate. It gave a very good leather. Regarding bleaching and pretanning too the condensed cresol sulphonic was found to be very satisfactory.

Novolac syntan prepared at the Central Leather Research Institute gave a leather, from cowhide, having shrinkage temperature of 85°C. and degree of tannage 62. A very full and tight leather was produced with light pinkish appearance which, however, gave a very fine colour after myrobing. Regarding its suitability for retanning, it was found to be quite comparable to wattle, quebracho or cutch. Chrome-retan leathers were produced in the Institute and were found to be as good as leathers produced with the vegetable materials.

Both the types of syntans *viz.*, Neradols and Novolac have enormous prospects in leather industry of India. One of the main types of leathers produced in India is E.I. tanned kips and sheep. Novolac type syntans have also been used with success at the Central Leather Research Institute for retanning of chrome tanned leathers. More and more syntans are being used for bleaching purposes. Majority of the cowhides received by the tanners are very poor in substance. Naturally, the leather produced from these hides are not fit for upper leathers for military boots and shoes. So, if the Novolac syntans are used in the production of chrome-retanned leathers for thepurpose, positive results will be achieved.

SYNTHETIC TANNING MATERIALS AND THEIR IMPORTANCE FOR THE INDUSTRY OF VEGETABLE TANNED LEATHER IN INDIA

BY

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ABSTRACT

A review is given on the development of syntans, their classification and their technical uses outside and inside India. Especially stressed are the possibilities to economize vegetable tanning processes in India by the use of replacement syntans in combination with cheap indigenous vegetable tanstuffs.

The first syntans which found a technical application in the leather industry were discovered by Stiasny[1] in 1911 in an endeavour to synthesize products with the tanning properties of vegetable tanning materials. Stiasny recognised that the tanning effect of vegetable tanning materials is related to the size of the tannin molecule and the existence of an aromatic configuration containing hydroxyl groups in these molecules. Without a too intimate knowledge of the institution of the different vegetable tannins he combined small aromatic molecules with hydroxyl groups, like phenol and cresol, to bigger ones by reaction with formaldehyde. To achieve solubility in water, essential for the tanning processes industrially developed, he introduced sulpho groups into the resins he had got in the way mentioned.

Stiasny's syntans reacted with pelt especially if the pH of the solution was kept low. Their acid sulpho groups combined with the basic groups of the collagen. The pelt was transferred into a substance which showed some properties of leather, but without the fullness and handle usually got by vegetable tannins. Today we classify Stiasny's tanning materials as auxiliary syntans. These syntans were introduced to the leather industry by Messrs Badische Anilin-und Sodafabrik, and found a use in vegetable tanneries, after some difficulties in the practical application had been overcome.

In combination with vegetable tannins they accelerated the penetration of these materials into the pelts, dissolved phlobaphenes and brightened the colour of the leathers.

Up to the end of the twenties the work of the research chemists in the field of syntans concentrated on making use of cheap raw materials for the production of auxiliary and combination syntans and on the collection and evaluation of technical experience in their application. At the beginning of the thirties a new group of syntans was made available for the tanners. The Geigy AG[2] introduced condensation products from dihydroxy diphenylsulphones for the production of white leathers without the help of other tanning materials.

On the other hand, research, started in Leverkusen in 1926, resulted in the discovery of a synthetic material without hydroxyl groups suitable for producing a pure white fully tanned leather. Huismann and Mauthe[3] found in the Leverkusen factory of the I.G. Farbenindustrie AG. that organic sulphonic acids containing aromatic rings without hydroxyl groups connected by—SO_2—NH—links had a good tanning effect.

The examination of a large number of such chemicals for tanning purposes revealed interesting information on the relations of chemical constitution and tanning effect. The influence of the molecular size, the content of sulpho groups and the content of so-called active tanning groups on the tanning properties of the synthetic compounds was studied especially by Mauthe and Noerr. Soon it was possible to make use of these studies for the production of synthetic tanning materials with good tanning properties from relatively cheap chemicals like phenol, cresol, naphthol, sulphuric acid and formaldehyde as well as from ligninsulfonic acids and cheap natural resins.

It was possible too, to exploit these studies to create new syntans with specific tanning effects. Whilst a vegetable tanstuff can be influenced in its tanning properties only within narrow limits, for instance, by sulphiting or by "sweetening," the synthesis of tanning materials allows the creation of tannins with specific effects, for instance, imparting a firm, or on the contrary, a soft handle to the leather, giving a specific colour, having a pronounced effect on the penetration of the tannin into the leather.

In the middle of the thirties two new syntans, Tanigan extra A and Tanigan extra B, made possible by the work of Mauthe and Noerr[4, 5] of Leverkusen, were introduced by I.G. Farbenindustrie to the leather trade. These new syntans has full tanning properties and showed much difference in their tanning effect compared with the auxiliary types of syntans known before. Therefore it seemed advisable to classify these different materials in regard to these properties. Three main groups of syntans might be so distinguished :

1. Syntans for production of white leather (for instance Tanigan supra brands of the former I.G. Farbenindustrie A.G.)
2. Replacement syntans (for instance Tanigan extra brands of the former I.G. Farbenindustrie A.G.)
3. Auxiliary and combination syntans (for instance Tanigan brands of the former I.G. Farbenindustrie A.G.)

As mentioned by Subramanian[6] at the symposium on the East Indian Tanning Industry in Madras in 1955, the auxiliary syntans especially, and the bleaching syntans in particular, have found a good market in South India. As the colour of E. I. goat, sheep and kip is very important for their market value, bleaching of the leathers after tanning has become an important operation, above all if besides avaram bark, other tanning barks or extracts have been applied during the tannage. A number of bleaching syntans are used by the tanners, for instance Perfectan C, Tanigan BLI, Tanigan BL and Basyntan FCBI.

Subramanian[6] further stated three years ago that replacement syntans are of less importance for the E.I. tanning industry. But it might be to the benefit of the Indian tanner to study the advantages of the application of replacement syntans utilized in other countries by evaluating from laboratory tests and the practical application of certain replacement syntans under Indian conditions.

On the European continent during the war, replacement syntans had become one of the main sources of tannin and were used in a high percentage together with locally available barks and extracts, such as pine, chestnut and oak. Especially in Germany a substitution of 25–50% of vegetable tannins by replacement syntans was normal. As, from 1949, the import of vegetable material into Germany was possible again, the consumption of replacement syntans by the tanneries decreased. The vegetable material was cheaper calculated on pure tannin and competition forced the tanners to supervise their costing attentively. But the sole use of vegetable tanning material resulted in some consequences which had been nearly forgotten by the tanners during years of combined application of replacement syntans and vegetable tannins.

The penetration of the tanning liquors was slower than it used to be, the colour of the leathers darker, the sludge and mould formulation in the pits much greater and, leading to higher losses of tanning material by sludge formation and enzymatic decomposition ; a higher percentage of pure tanning material calculated on pelt weight had to be used to get the same yield as before.

So, very soon the German Leather industry was again purchasing replacement syntans and the reason, curiously enough, was again to keep the cost of tanning down. Whilst during the war the interest of the leather industry was directed towards the replacement of hardly available vegetable materials at rates dictated by the scarcity of the latter, now the tanners started to exploit the special effects of certain replacement syntans on vegetable tannins :

1. The property to dissolve phlobaphenes and other precipitates in the tan liquor still usable for tanning.

2. The property to inhibit the destructive enzymatic action of moulds on vegetable tannin.
3. The property to accelerate the penetration of the tan liquor into the pelt.
4. The brightening effect on the colour of the tanning solutions.

In other words ; the tanners reduced their losses of vegetable tanning material during tanning (1 and 2) by a reasonable substitution of their vegetable tannins by replacement syntans, accelerated the tannage to cut the overheads per unit of leather produced and to get a quicker return of their money invested in raw hides (3) and, in addition, increased the sales appeal of the leather (4).

It is a known fact that a considerable part of pure tannins bought by the tanner is lost during the operations in the tannery and is not sold in the form of leather. If we exclude the losses due to incomplete leaching of the barks, fruits etc., the main losses are due to enzymatic decomposition, precipitation by dilution, hardness of water and, of course, some tanning material will disappear in waste liquors.

Losses in vegetable tanning material happen both when catechol tannins and pyrogallol tannins are used. Catechol tannins show a tendency to form compounds of little or no tanning value as a result of enzymatic effects, oxidation and chemical condensation. These compounds are known as phlobaphenes, which precipitate in the form of sludge during the tannage and which are normally not incorporated into the pelts. Some tanning materials of the catechol group, for instance, quebracho, contain particles already in the fresh extract which are soluble in hot liquors, but precipitate when the liquor cools off.

Losses in tanning materials are especially large if pyrogallol tannins are used. It is widely known, that myrabolam liquors are particularly sensitive to enzymatic decomposition. Within eight weeks 50–60% of the pure tannin of myrobalam liquor may be lost for this reason. As there have been no publications available on losses in Indian tanneries, some figures resulting from investigations in other places may give an indication of the losses actually found in vegetable tanneries.[7]

Table I

Losses of tannin (Percent)	Remarks	Author
20		Parker[8]
35	Pit tannage	Grasser[9]
38	Drum tannage	Grasser[9]
13	Ukrainian sole leather factories	Goldenberg[10]
30–35	Pit tannage	Weisberg[11]
15–20		Weisberg[11]
26–28		Fiksl[12]
36	Hungarian sole leather factories	Jany[13]
39	Leather factory Wolfner	Wodnyansky[14]

It is obvious that differences in the composition of the vegetable tannin mixture, in the local tannery conditions etc. influence the figures and explain the differences above. However, the different authors agree that more than half of the losses are due to chemical changes in the liquors and to sludge formation. A paper by Petrie[15] shows, that recently also considerable losses in modern tanning processes have been found. Of a total loss of 20%, 14% is due to enzymatic decomposition and the formation of sludge. Also investigations by Van Vlimmeren[16] show losses in modern Dutch tanneries up to 40%.

It must be borne in mind that the composition of European tan liquors generally is different from the blends used in India. Avaran, konnam, babul and goran are not used at all in Europe and myrabolams in the form of fruits or extracts are used only in small percentages in spite of their low price. As the myrabolam tanning material is especially sensitive to decomposition a tannery using a considerable amount of myrabolam extract might certainly have still bigger losses of tanning material than stated by the above mentioned authors.

For the Indian tanner who follows the development of the leather industry outside India the question arises : Is it advisable for economic and quality reasons under present Indian conditions to develop tanning methods using replacement syntans ?

Of course there is interest in good colour of E.I. leathers as well as of sole leather.

There is also an urgent desire to cut down the tanning time. If we look first at the conditions in the tanneries producing E.I. sheep, goat and kip leather, we will find that these tanneries develop only to a certain optimum size. It is more economic for a proprietor of a tannery to buy or rent another unit, if he wants to increase production, than to enlarge an existing one over the optimum size.

However, the administration of different units means increase in overheads and every suggestion for producing more leather in one already existing unit is of interest to the tanner. This can be done by shortening the tanning time without lowering the quality of the leathers by substituting part of the vegetable tanning material by replacement syntans. No basic changes in the established tanning methods are essential.

T. G. Sane, for instance, made a technical test in India with heavy goat skins and reduced the usual tanning time by 20% by replacing a part of imported vegetable tanning material by Tanigan extra KNS, otherwise strictly following the traditional method of tanning E.I. skins. There was not only no loss in weight, but a considerable gain by better utilisation of the vegetable tanning material. That means that it is possible to cut down the tanning time still more, if only the usual weight of the skins is to be achieved.

E. I. tanners generally work with a two pit system of low concentrated liquors.

If, as usual in modern sole leather tannage, a pit system with increasing strength of liquors is used, of course much faster tanning is possible, not to speak of acceleration by the use of pretanning methods and drums.

But, if pit tannage alone is considered, it is possible under Indian conditions to tan sole leather from buffalo hides of normal size within 12 days tanning time to a good quality for the Agra market by use of the accelerating properties of replacement syntans like the Tanigan extra KNS mentioned.

In the tests mentioned the substitution of vegetable materials was done by replacing a part of imported extracts, so that the amount of foreign exchange needed to cover the costs of the tannage was approximately on the same level as usual.

It might even be possible to use a larger amount of cheap, locally available tanning materials than usual, if the properties of certain replacement syntans are exploited for tannage. It is well known that myrabolam tannin in the form of nuts and extracts is available in abundance in the country. Its use for the tannage of thick sole leather, however, is limited, as the myrabolam tannin alone will not penetrate thick pieces of pelt, and even when blended with other materials like wattle, babul, goran etc. the practical tanner generally avoids using more than 1/3of the mixture in the form of myrabolams in order to slow down too much the penetration and to avoid case hardening or a too spongy leather.

Laboratory tests conducted in the Leather Department of Farbenfabriken Bayer A.G., in Leverkusen showed that a mixture of 60 parts pure tannin of myrabolams and 40 parts of pure tannin of babul produces a leather with a lower content of fixed tannin compared with a test under the same conditions with a mixture of 35 pts. myrabolam and 65 pts. babul. However, when in the first mixture 10–20% of the pure tannin was substituted by a replacement syntan, an even higher percentage of tanning material was bound to the hide substance. As an analytical investigation of the leathers revealed, the centre layers of the leather especially showed a higher percentage of fixed tannin.

These results might be explained partially by the fact, that the myrabolam tannin belongs to the group of the pyrogallol or hydrolysable tannins. Chemically, these tannins are esters of sugars and aromatic acids, such as gallic acid and other acids formed by enzymatic dehydration of gallic acid, like chebulic acid, brevifolincarbonic acid, dehydrogallic acid etc.

The ester link might be split up very easily, for instance, by enzymatic action. Such enzymes are above all produced by micro-organisms, such as various moulds, like *Aspergillus niger* and *Pencillium glaucum*, which use the sugar part of the hydrolysable tannins as food.

The decomposition products or the compounds formed out of these decomposition products are not real tanning materials any more.

For the practical tanner it might be of special interest that it is very difficult to prove exactly how far a myrabolam tanning liquor has lost its tanning content through enzymatic decomposition, as products resulting from the splitting up of the myrabolam tanning might be bound by hide powder during the standard tannin analysis, but have no real leather forming properties. Komarek[17] proved that by substituting 30% of a myrabolam extract by decomposition products of myrabolam tannins like gallic acid and glucose with no tanning activity the analysis figures remained nearly unchanged, compared with the original extract.

Table 2

		Tannin (Percent)	Non-tannin (Percent)
I.	Myrabolam extract	68.4	23.5
II.	90% Myrabolam extract (as I)	68.4	23.3
	10% gallic acid/glucose 68,4 : 23.5		
III.	80% Myrabolam extract (as I)		
	20% gallic acid/glucose 68.4 : 23.5	68.1	23.9
IV.	70% Myrabolam extract (as I)		
	30% gallic acid/glucose 68,4 : 23,5	67,8	24.3

Komarek[17] showed further that an increasing addition of gallic acid and glucose to a myrabolam extract, as mentioned above, very much reduced the quality of the leathers produced with the liquors in spite of the same analysis figures.

The above mentioned laboratory tanning test showed that a leather tanned with babul and myrabolams in the ratio of 40 : 60 had less fixed tannin than a leather made with babul and myrabolam in the ratio 65 : 33 under the same tanning conditions. A relatively small replacement of the pure tannin in the first mixture by replacement syntans, however, produced a leather with more fixed tannin. The fixed tannin bound comparatively evenly through all the layers of the leather.

This might only be explained by the inhibiting effect of the replacement syntans used, on the development of mould in the liquors and by the accelerating effect of these syntans on the penetration of the vegetable tanning materials into the leather. Of course, mould in tan liquors can be prevented also by other means. However, as Komarek[17] has stated, the usual fungicides not only prevent mould, but generally influence all the microbiological processes, in the tan liquors. Above all the necessary acid formation by fermentation might be influenced unfavourably by an overdose of the generally very effective fungicides, which might even be caused involuntarily by an accumulation of these fungicides in the course of time in the liquors. In contrast to the continuous uptake of the replacement syntans out of the tanning system fungicides might accumulate there.

So at present the inhibiting effect on mould growth of certain replacement syntans recommends itself for evaluation in the tanyard, especially as these replacement syntans show other good effects, already referred to, on the economics of the tannery.

It seems obvious that the use of a reasonable percentage of replacement syntans could allow a better utilisation of myrabolams, the only tanning material, which is at present available in India plentifully and easy to collect. So it might be an interesting task to gather more details, above all from tanning tests under practical conditions, on this problem, which would be interesting not only for the tanners in India, but also in foreign countries, where the application of Indian myrabolams is still limited to very small quantities. After everything that was said at the Calcutta Symposium in 1958, there seems to be a possibility to collect more myrabolams in India for the benefit of the Indian tanners and to obtain foreign exchange, if only more suitable methods for making use of this tanstuff are developed. The combined application of vegetable mixtures containing a high amount of myrabolams with a suitable quantity of replacement syntans is apparently a promising way.

It might be stressed here also that other Indian tanning materials of the mangrove type can be exploited for increased practical use by combination with replacement syntans, as B.B. Roy, N. N. Guha and P. Choudhury[18] of the Bengal Tanning Institute have shown by combining mangrove for tanning tests with Tanigan extra KNS.

In this paper not all the possibilities of applying syntans in vegetable tanneries could be discussed exhaustively, due to the limitations of time.

However, the facts discussed may perhaps be of particular interest for the leather industry of this country.

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COMPLEXES OF HEXAMETHYLENE TETRAMINE AND PHENOLS IN TANNING

BY

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ABSTRACT

A number of complexes having good tanning properties have been prepared from hexamethylene tetramine and phenolic compounds. While hexamethylene tetramine alone has little or no tanning properties, the complexes obtained by treatment of hexamethylene tetramine with resorcinol, pyrogallol, catechol, etc., exhibit good tanning properties. The complex obtained from phenol offers a sharp contrast in that it has no tanning action. The optimum conditions of tanning with resorcinol-hexamethylene tetramine complex have been studied. In this type of tannage, hexamine acts as a donor of formaldehyde under various pH conditions.

Introduction

During the past hundred years, hexamethylene tetramine[1] has been attaining more and more commercial importance. This increasing interest is due to the divergent properties possessed by this compound.

Hexamethylene tetramine forms simple addition complexes with a number of metallic and non-metallic compounds by virtue of its weak tertiary basic nature. It has found extensive application as a donor of formaldehyde to which it could be easily hydrolyzed. Hexamethylene tetramine forms a number of resins with a variety of compounds.

In view of the divergent properties possessed by this compound it was deemed of interest to study its reaction on pelt. While hexamethylene tetramine exhibited no tanning characteristics the molecular compound made from resorcinol and hexamethylene tetramine was found to have good tanning action.

Preparation

The complex was prepared by mixing saturated aqueous solutions of resorcinol and hexamethylene tetramine. The complex which separated immediately was purified by crystallisation from methanol.

Tanning

Generally tanning was done by immersing the pelt in an aqueous solution of the complex for a period of 40 hours with intermittent shaking. The tanning was found almost independent of pH from 7 downwards. Above pH 7 the complex did tan to give a dark coloured leather but the time taken for tanning was from 15 to 20 days. The leathers produced at all pH values from 2–10 had high shrinkage temperatures ranging from 94–98°C.

Properties of leather

The properties of resorcinol hexamethylene tanned leather can be enumerated as follows : mellow, tight, full, strong, tan or light brown colour, poor light fastness, absorbs oils and grease readily, not easy to dye, stable to acids, tendency for a drawn grain and lastly a high hydrothermal stability.

Other phenols

Among the phenols tried the complexes from resorcinol, catechol and pyrogallol only had tanning action. It was observed that the more stable complexes had less tanning action. For example, there is a wide disparity in the properties of the phenol hexamethylene tetramine complex and resorcinol hexamethylene tetramine complex. While the phenol complex is very stable both in boiling water and boiling 50% acetic acid the corresponding resorcinol complex undergoes rapid polymerisation on keeping it in moist condition, boiling with water and on boiling with 50% acetic acid for 30 seconds.

Hydroquinone, phloroglucinol and the cresols did not form complexes and a complex formed from β-Naphthol tanned only with difficulty.

Mechanism of tanning—Mannich reaction

Preliminary experiments showed clearly that the tanning is essentially brought about by resorcinol and formaldehyde formed by cleavage of the complex. This is quite conceivable in view of the fact that hexamethylene tetramine is known to behave as a donor to formaldehyde under certain conditions. From a theoretical standpoint the outstanding property of the leather is its high hydrothermal stability and any mechanism put forward must account for this property.

In 1952, Windus[2] found that a leather having a high shrinkage temperature was obtained by treating pelt with resorcinol and formaldehyde. He postulated without giving any experimental evidence that the high hydrothermal stability of the leather is due to formation of Mannich type of linkage. In view of the similarity between the resorcinol hexamethylene tetramine complex tannage and resorcinol-formaldehyde tannage it was considered quite probable that a same kind of reaction was taking place in this case also.

Experiments employing the complex and collagen, deaminised collagen and ultramide 6-A, under a variety of reaction conditions showed that the resorcinol and formaldehyde combined in an irreversible way with mainly the primary amino groups of collagen. This supports the idea of formation of Mannich linkages.

Experiments employing resorcinol, formaldehyde and collagen showed that such a reaction takes place at almost all pH levels from 2–6 and that the fixation was most at pH 5, where polymerization was least. This fact is well in accordance with the principles of the Mannich reaction, since it involves dual catalysis in an amphoteric medium.[3] Strong acidic or alkaline conditions make the formation of Mannich linkages a bit difficult. The fact that the shrinkage temperatures of the leathers produced at various pH levels were almost the same shows clearly that the extent of Mannich linkage formation is no criterion for the boosting up of shrinkage temperature.

It was also found that the better leather produced at pH 2 in experiments carried out by Windus[2] was not entirely due to the extent of Mannich reaction but was due to the combined effect of the reaction and polymerization. The fact that the same type of leather (or even better) could be made by doing the tanning initially at pH 5 and then acidifying the medium to pH 2 confirms the above hypothesis.

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DISCUSSION

Mr. S. C. Nandy (C.L.R.I.) : Were the physical properties of leather produced by tanning with hexamethylene tetramine resorcinol complex tested ?

Mr. S. Ranganathan : Quoted Dr. Windus as saying that the linkage was 10 times that of vegetable tanning assuming vegetable tanning to be through H-bonding.

Dr. S. K. Barat : Since the actual practice on the Continent is to use formaldehyde directly, what is the particular advantage in using hexamethylene tetramine as a donor for the formaldehyde ?

Mr. S. Ranganathan : Resorcinol and formaldehyde were used for tanning even earlier to 1952. The ratio recommended by the authors of the present paper was formaldehyde : hexamethylene tetramine as 1 : 3. The advantages are controlled liberation of formaldehyde and leather of high T_s.

CHROME RETAN LEATHERS : USE OF INDIGENOUS TANSTUFFS : PART I

BY

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ABSTRACT

A study was made on the use of indigenous tanning materials in the retanning of chrome upper (chrome retan) leathers. The effects of the nature and amounts of vegetable tanning materials, fats, oils and waxes used on the chemical and physical characteristics of fine leathers were studied and reported.

The method of leather manufacture by chrome-retan process is highly developed in U.S.A. This involves chrome tanning followed by vegetable tanning.

Since in India most of the raw hides are procured from the fallen stock, work was taken up at this Institute to develop some methods for processing the fallen stock of hides by 'Chrome-retan' to make fuller and thicker leather suitable for civilian and military needs.

A study on the optimum conditions for tanning indicated that unhairing in two stages—first with lime then followed by treatment with sodium sulphide in a separate bath gave better results.

The limed hide is delimed and subsequently pickled following traditional method.

Studies on chrome tanning indicate that anionic chrome reduces fixation of vegetable tannin while cationic chrome increases. Cationic chrome tanning with 3.5% sodium bichromate, on the weight of the pelt, is found to be the optimum for the process of 'chrome-retan.'

The neutralisation of chrometanned leather with molar solutions of different neutralising agents, namely $NaHCO_3$, Na_2CO_3, NaOH, $Na_2S_2O_3$, sodium acetate, borax, and sodium formate has shown that sodium acetate and $NaHCO_3$ give the best result. $NaHCO_3$ proved to be the best for heavy upper leathers and military boot leather and sodium acetate for the civilian upper leathers.

Experimental

Retanning : The butt portions of hides chrometanned under identical condition, are after neutralisation, washed well to remove the neutral salts from the surface of the pelt and subsequently retanned with various tanning materials.

In this experiment tan liquors of specific gravity 20°BK were prepared and used for retanning in all the cases.

The leathers thus produced are aged overnight on horse and next day washed, air dried and finally analysed. The results obtained from these experiments are quite promising and they are given in Table I.

It is evident from the table that indigenous tanning materials have prospects in the manufacture of chrome-retan leathers.

Discussion and conclusions

According to their suitability for the process of chrome retan, wattle (Nilgiri), wattle (S.Africa), Goran and Karada come under the first group, Babul, White velam and Arjuna come under the second group and Konnam, Avaram, Myrobalam and Divi-divi come under the third or last group.

The study on retannage with vegetable tannin has been conducted to develop some processes for the manufacture of fuller, tighter and thicker leathers from the fallen hides. Judged from that angle of view it is found that mellow tanning materials, namely avaram, konnam, etc., are unsuitable for the purpose. Moreover, they have got great demand for our well established E.I. tanning industries.

Divi-divi and myrobalam also are found unsuitable. But as we have got an excess supply of myrobalam this material may be tried in combination with other catechol tanning materials. Materials in the second group, *i.e.*, babul, white velam, arjuna, etc., give medium degree of tannage ; per cent increase in thickness is also in between those obtained with Group I and Group III. Arjuna and babul produce a slightly cracky grain also.

Materials of Group I, *i.e.*, wattle (Nilgiris), wattle (S.Africa), goran, hopea and karada are found suitable for 'chrome retan' process, of which goran is considered to be the best. It is found to produce almost all the properties desired for chrome-retan upper leathers, *i.e.*, reasonable degree of tannage with increase in thickness and reasonably higher shrinkage temperature with good tensile strength.

Babul and Arjuna may be made to produce suitable leather if mixed with some mellower tanning materials or after treating with bisulphite of soda prior to use for retanning.

Hence it is assessed that indigenous tanning materials—Hopea, goran, wattle and karada—have bright prospects in the manufacture of chrome retan upper leathers.

The preliminary assessment being over experiments were conducted on retanning varying (1) the variety of suitable tan material, (ii) the amount of pure tan, (iii) concentration of pure tans, (iv) time of vegetable retanning, (v) T/Nontan ratio, and (vi) pH value.

The experiments were conducted under identical conditions with only one variable at a time and the results obtained thereby in all the above mentioned cases were as follows :

(i) As already mentioned, goran was found to be the best of the indigenous tanning materials for the purpose of chrome retan. Karada was found to be next to goran.

(ii) 10 to 15% of pure tannin was found to be sufficient for the different types of chrome retan upper leathers.

(iii) It was found that concentrated liquor penetrated quickly.

(iv) Upto certain limit, the greater the time the higher the percent fixation but it was not very appreciable.

(v) Ratio of T/NT had no influence on per cent fixation of the organic matters. There was no appreciable change in fixation when the ratio of tannin/non-tannin was adjusted to different levels by adding gallic acid to a known amount of pure tannin.

It was found that the results obtained here did not strictly follow the order of astringency established by Barat and Das.[1] On the basis of percent fixation of organic matters their order was as follows : Konnam, Avaram, Babul, Goran (Myrob). In our study the order is as follows :

Babul, goran, karada, myrobalam, avaram and it is clear that babul, myrobalam and goran follow their order. (Higher the astringency higher the percent fixation).

(vi) pH of vegetable tanning liquors was found to have no appreciable effect on the percent fixation of organic matters which was mainly responsible for the improvement of bellies and shanks. pH of the tan liquor had great bearing on the penetration of the tannin, higher the pH quicker the penetration of tannin.

Having fixed these optimum conditions, chrome retan upper leathers have been manufactured on small tannery scale. Repeated processing of hides by the chrome-retan method has proved highly successful on pilot plant scale too.

Finally it was found that for the manufacture of heavy upper leathers, namely work boots, chappals and military boots leather liquors of higher specific gravitiy were suitable ; these were not obtainable from goran and karada bark. The leaching of the barks with hot water was found to give liquors suitable for civilian upper leathers only.

Name of Vegetable Tannin used	T/NT ratio	Degree of Tannage	Fibre structure under microscope	Ten-sile strength	Vegetable penetration with respect to its total thickness	Percent increase in thickness
Arjuna	2.0	41.31	Slightly loose (brittle fibres)	3125	2/3rd	8.66
Goran	4.0	46.78	Loose	3419	3/4th	16.00
Babul	1.5	36.34	Very loose	3537	2/3rd	18.96
White velam	2.4	35.22	Fairly compact	4958	2/3rd	17.40
Hopea	4.0	50.69	Compact (brittle fibres)	4775	2/3rd	16.00
Karada	2.5	50.67	Loose	2500	Full	10.14
Wattle (South Africa)	3.0	50.37	Loose	3105	Full	18.83
Wattle (Nilgris)	3.0	41.71	Slightly loose	3833	3/4th	18.98
Avaram	1.7	28.50	Do.	2969	Full	10.14
Konnam	0.8	34.90	Fairly compact	4312	Full	8.00
Myrobalam	2.3	33.89	Do.	5000	Full	9.60
Divi-Divi	1.2	32.60	Slightly loose	4284	Almost full	13.03

For the manufacture of heavy upper leathers cutch extract (Indian), quebracho and wattle extracts were utilised under identical conditions. It was found that cutch extract produced the best results, which would be evident from the Table II annexed herewith.

The analysis of the leathers was done according to the A.L.C.A. method for chrome-retan leathers.

The results obtained were as follows :

Percentage moisture	14.8 to 16.0
Percentage Cr_2O_3	2.25 to 2.50
Percentage hide substance	55.0 to 60.0
pH of water solubles	3.4 to 4.0
Percentage water solubles	1.5 to 3.0
Percentage total ash	2.0 to 2.7
Percentage fats and oils	3.0 to 4.0
Thickness of the finished leather	2.2 to 3.0
Increase in thickness	15.0 to 20.0%
Area shrinkage (over chrome shaved sample)	Almost nil.
Shrinkage temperature varied from	110° to 112°C

	Sample parallel to the line of backbone	Sample perpendicular to the line of backbone
Tensile strength	2500 to 2900	2700 to 4100
Elongation at break	29.4 to 35.3	36.5 to 44.7
Tearing strength	143 to 206	119 to 199

Fatliquoring and Stuffing : Different types of fatliquoring and stuffing have been tried as follows :—

(*a*) Fatliquoring with	Sulpholin oil—P/Fish oil.
(*b*) ,,	Sulpholin oil—P Fish oil Bar soap
(*c*) ,,	Sulpholin oil—P Pungam oil
(*d*) ,,	Sulphated Pungam oil Pungam oil
(*e*) Stuffing with	Tallow Spindle oil Yellow grease
(*f*) ,,	Tallow Fish oil

RESULTS OBTAINED FROM DIFFERENT TYPES OF RETANNAGES (Cutch, Quebracho, Wattle, Myrab, etc.)

General appearance	Feel of leather	Fullness in Butt	Fullness in shank	Crackiness of grain			Tensile strength	Tightness	Name of the vegetable tannin used for tanning
				Single fold	Double fold	Key Test			
(a) *Heavy Upper Leather*—									
1. Very good	Soft and nice.	Full and round.	Full	No	No	No	Very strong.	Very tight	Cutch Extract No. 2 (Indian).
2. Good	Do.	Do.	Do.	Do.	Do.	Do.	Do.	Tight	
3. Good	Do.	Do.	Slightly less	Do.	Do.	Do.	Do.	Very tight	
4. Fair	Do.	Do.	Do.	Do.	Do.	Do.	Do.	Do.	
1. Good	Soft and mellow.	Do.	Full	Do.	Do.	Do.	Do.	Do.	Quebracho Extract (Foreign).
2. Good	Do.	Do.	Less full	Do.	Do.	Do.	Do.	Tight	
3. Fair, ticky belly	Do.	Do.	Full	Do.	Do.	Do.	Do.	Do.	
4. Do.	Do.	Do.	Do.	Do.	Do.	Do.	Do.	Do.	
1. Very good	Soft	Do.	Do.	Do.	Do.	Do.	Do.	Very tight	Wattle Extract (Foreign).
2. Good	Do.	Do.	Do.	Do.	Do.	Do.	Do.	Do.	
3. Good	Do.	Do.	Do.	Do.	Do.	Do.	Do.	Tight	
4. Fair	Slightly firm.	Do.	Full but sheety.	Do.	Do.	Do.	Do.	Do.	

(b) *Light Upper Leathers*—

1.	Better	Firm	Full and round.	Full	No	No	No	Strong	Tight	Cutch Extract No. 2 (Indian).
2.	Good	Do.	Do.	Do.	Do.	Do.	Do.	Do.	Do.	
3.	Do.	Do.	Do.	Do.	Do.	Do.	Do.	Do.	Do.	
1.	Very good clear grain.	Soft	Do.	Do.	Do.	Do.	Do.	Very strong.	Do.	Goran (Indian).
2.	Do.	Do.	Do.	Do.	Do.	Do.	Do.	Do.	Do.	
3.	Do.	Firm	Do.	Do.	Do.	Do.	Do.	Do.	Do.	
1.	Fair, defeted grain	Soft but belly flat and tiny	Full and round.	Less full	Do.	Do.	Do.	Strong	Do.	Myrab Extract (Indian).
2.	Good	Do.	Full	Papery	Do.	Slight	Do.	Do.	Do.	
3.	Do.	Soft	Full and round.	Less full	Do.	No	Do.	Do.	Do.	
1.	Fair	Firm	Full	Full and sheety.	Do.	Slight	Do.	Do.	Do.	Gambier Extract.
2.	Fair	Do.	Do.	Not so full.	Do.	Do.	Do.	Do.	Do.	
3.	Good	Soft	Full and round.	Full	Do.	No	Do.	Do.	Do.	
1.	Do.	Do.	Do.	Do.	Do.	Do.	Do.	Do.	Do.	Quebracho Extract (Foreign).
2.	Do.	Do.	Do.	Do.	Do.	Do.	Do.	Do.	Do.	
3.	Do.	Softer	Do.	Do.	Do.	Do.	Do.	Do.	Do.	

The operation of fatliquoring was done under identical conditions and it was found that in all cases the surface of the leather was free of oil and consequently felt harsh ; most of the leathers were hard and cracked on double fold.

The stuffing was by hand and it was clear that recipe (*e*) was better than recipe (*f*).

Finally, a double bath fatliquoring was followed by drumming the leather first in an emulsion of sulphated mineral oil such as sulpholin oil—P and free fish oil and secondly treating the leather in a separate bath of free Fish oil dispersed with cationic dispersing agent namely—Fixonal V. R. or Triton K–60.

The leathers produced have been examined at our Institute and the conclusions drawn thereby are as follows :—

(*a*) The usual type of fatliquors used for full chrome upper leathers are found unsuitable for the chrome retan upper leathers, even on increasing the amounts. This is to be expected because of the special character due to chrome in the central layer and mixture of chrome and vegetable on the surfaces.

(*b*) Double bath fatliquor has been proved to be suitable as it produced the soft, firm springy nature with non-cracky grain, even on double fold. This is so because the first fatliquor is of the nature usually used for chrome upper leather and consequently it could lubricate the chrome layer in the centre. This would not combine with the grain and flesh layer because of the different characteristics of these. The second fatliquor because of its specific nature is precipitated after a few minutes and combines with the grain and flesh layers.

Most probably the second fatliquor is responsible not only for the lubrication of the mentioned layers but for the non-cracky nature of the grain too.

(*c*) Both the stuffing mixtures have been found to be alright but the recipe (*e*) was found better for the military boots upper and works boot leathers. Leathers made with the recipe (*f*) contain more grease on the surface ; this is not used in our hot climate as the grease would melt and make the dress of the wearer dirty. This may be used only in colder regions of our country. The leathers may also be used as chappal straps ; the leather produced by the recipe (*e*) was quite good, non-greasy on the surfaces and possessing all other desired properties of chrome retan upper leathers.

Finally, it was concluded that the double bath fatliquoring was quite satisfactory for the heavy upper leathers—military upper leathers, works boots and chappal and the leathers produced by stuffing recipe (*f*) were found to be suitable for military boots leathers and heavy upper leathers.

The analysis figures given below for chrome retan leathers meant for military boots show that they are quite comparable to the specifications laid down by U.S. defence organisation. This type of leather is extensively used in the United States.

Calculated on Hide substance basis	U. S. specification	Our leathers
(i) Content of chrome in the form of Cr_2O_3	4—5%	3.5 to 4.25
(ii) Fats and oils	25 to 30%	33%
(iii) Vegetable tannins	38 to 46%	30 to 35%
(iv) Thickness in m.m.	1.8 to 2.25	2.2 to 3.0
(v) pH of water solubles	3.1 to 3.5	3 to 4

ACKNOWLEDGEMENT

Thanks are due to Mr. M. A. Ghani, Senior Scientific Officer, Control Laboratory and Mr. K. T. Sarkar, Senior Scientific Officer (Tannery), who tested the produced leathers on laboratory scale and commercial scale manufacture.

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CHROME RETAN LEATHERS—USE OF INDIGENOUS TANSTUFFS

PART II

by

S. P. SINGARAM AND Y. NAYUDAMMA

(Central Leather Research Institute, Madras)

ABSTRACT

Several indigenous tanstuffs were tried for retanning chrome leathers meant for uppers. The combining value, tan value and water soluble contents, were determined. Similarly the increase in thickness on retanning was noted. From these results, the suitability of indigenous tanstuffs for retanning of chrome upper leathers was assessed.

This type of combination tannage of prechroming followed by retanning with vegetable tan materials has got certain advantages and improved properties over that of independent chrome or vegetable tanning. Defence Services of India require military boots and other leather accoutrements which must be made of leather of stringent military specifications as regards thickness and strength. It has always been difficult to make army boot upper leather of the required thickness from Indian cowhides, which are mostly light and thin, by mere chrome tanning. The chrome retan process, however, gives thick leathers from thin hides. By developing the process using cowhides and vegetable tan materials available in India, a means of supplying essential upper leather for military boots will be provided.

Nearly 85% of the cowhides available for tanning are from dead animals. Civilian upper leathers manufactured by chrome tanning from these hides are of poor quality with loose and pipy grain. Chrome retanning, however, improves the quality by giving a tight grain in the shanks and belly portions where they are predominantly loose and increases the cutting value of the leather.

Choice of vegetable tanstuff used for retanning determines the quality of the leather produced. Among the indigenous tanning materials, it should be one having more filling and combining properties so as to get the desired thickness ; it should also possess sufficient astringency to produce a tight grained leather. Since crackiness of the grain is associated with retanning the tan material or its blend should be such as to give a non-cracking leather.

The water solubles present in the retanned leather, which include loosely combined tannins, gums and resinous matter from vegetable tanstuff, and insufficient fat-liquoring of the stock may account for the crackiness of the grain. So a study of tan value, combining value and water soluble content of the retan leather and the thickness of the leather has been made to select suitable tanstuffs for retanning.

Experimental

The following semi-micro method was used for the determination of tan and combining values.

Weighed unchromed hide powder, containing 1.0 gm dry matter is transferred into a 100 c.c. bottle fitted with a rubber cork. 25 c.c. of distilled water is added to the hide powder and the bottle shaken well for 2 hrs. in a shaker at 30–40 r.p..m, 1% and 6% tan solutions on pure tannin basis of the tanning material are prepared as for tannin determination and centrifuged. For extracts 1% and 6% tan solutions are prepared by dissolving the requisite amount and the tan content adjusted after determining the tan content of the liquor by usual analytical methods. As regards barks they are crushed and soaked in water to get the tannin infusion. The liquor was adjusted to 1% strength after centrifuging and to get 6% tan solution, the tan liquor was concentrated under reduced pressure using a vacuum pump. 25 c.c. of tan liquors of the respective strengths are added in 5 c.c. portions at ½ hr. intervals to the hide powder samples and the tanning is completed in 3 hrs. in the shaker at 30-40 r.p.m. The hide powder plus tannin solution is kept overnight and the following morning the liquor filtered off using a Gooch crucible. 5 c.c. of the original solution and 10 c.c. of the filtered solutions are separately evaporated to dryness in dishes to constant weight at 100°C. The difference in weight of the two residues multiplied by 5 is the tannin taken up by 1.0 gm of the dry hide powder and the value multiplied by 100 is the tan value.

To determine the combining value, all the hide powder from the bottle is rinsed out to the filter and washed with 500 c.c. of distilled water from an overhead reservoir over a period of 5 hrs. It is then dried at room temperature and then finally at 100°C. to constant weight. This weight minus 1.0 multiplied by 100 is the combining value (tannins taken up by 100 gms of dry hide powder).

In order to study the water soluble content of the retanned leathers produced with the various vegetable tan materials, postcard size pieces of chromed leathers with 3.5% Cr_2O_3 content were retanned with 20% tannins of each of the several tanstuffs, keeping the float 1:3 and at pH 4.5. The comparative increase in thickness produced by retanning with the same quantity of tanning materials at the same concentration and pH used for retanning, was noted.

All the pieces of retanned leathers were aged for 10 days and analysed for their water soluble hide substance and moisture contents.

The following are the results of tan value, combining value and water soluble content.

1% tan solution = 25% tannins on dry hide powder.

6% tan solution = 150% tannins on dry hide powder.

(Tan value—combining value) = Washables per 100 gms. of dry hide powder

TABLE I

		With H.P.			Retanned Leather		
Tanning material		Tan value	Combining value	Washables	Water solubles of Retan leather on 14% mixture	Hide substance	Water solubles per 100 gms. hide substance
Goran	1% solution.	25.4	22.9	2.5	0.999	60.43	1.519
	6% ,,	96.7	63.0	33.7			
Babul	1% ,,	22.5	19.4	2.9	3.055	59.32	4.817
	6% ,,	76.8	56.8	20.0			
Wattle	1% ,,	22.8	15.3	7.5	1.721	60.71	2.635
	6% ,,	89.3	56.3	33.0			
Karada	1% ,,	24.8	23.1	1.7	0.984	61.38	1.466
	6% ,,	93.4	56.2	37.2			
Avaram	1% ,,	21.5	12.2	9.3	2.275	60.39	3.467
	6% ,,	86.0	53.6	32.4			
Konnam	1% ,,	22.1	12.8	9.3	2.348	60.26	3.581
	6% ,,	96.8	60.4	36.4			
Quebracho	1% ,,	13.9	5.6	8.3	1.462	59.60	2.277
	6% ,,	62.6	40.5	22.1			
Cutch	1% ,,	18.2	11.5	6.7	1.464	59.70	2.277
	6% ,,	81.7	58.6	23.1			
Myrobalan	1% ,,	22.1	3.4	18.7	2.058	59.89	3.206
	6% ,,	86.8	39.6	47.2			
Divi-Divi	1% ,,	21.3	1.1	20.2	1.872	60.96	2.838
	6% ,,	89.7	33.0	56.9			
Gambier	1% ,,	19.4	Negligible	19.4	3.850	59.89	5.994
	6% ,,	99.0	38.6	60.4			

Discussion

From the results, it could be seen that the tan value, combining value and water soluble content are similar for certain of these tan materials; Goran and Karada; Avaram and Konnam; Quebracho and Cutch; Myrobalan and Divi-divi; this evidently shows the similarity of their behaviour in the mechanism of tanning and retanning. So instead of one, the other material in the group could be used alternatively either alone or in blend. Quebracho is a tanning material used extensively for retanning abroad. Cutch happens to be a suitable indigenous substitute and is proved to be so in commercial scale of retanning also.

The tan materials when arranged in an order of increasing washables with hide powder using 1% tan solution are Karada<Goran<Babul<Cutch <Wattle<Quebracho<Avaram<Konnam<Myrob<Gambier<Divi-divi.

When arranged in the order of giving increasing amount of water solubles in retan leather they are Karada<Goran<Quebracho<Cutch <Wattle<Divi-divi<Myrob<Avaram<Konnam<Babul<Gambier.

There seems to be a general tendency for the increase in the amount of washables (difference between tan value and combining value) to give increasing amount of water solubles in the retanned leather ; however in the case of babul smaller amount of washables gives more of water solubles in the retanned leather, while in the case of quebracho as also with myrobalan and divi-divi more of washables give less of water solubles. The discrepancy may be due to the difference in the behaviour of tannins and non-tannins of the different tan materials in their ability to form stable chromium complexes. In the former case the chromium complex formed by the babul tannins might be less stable so as to be removed by extracting while in the case of quebracho, it is easily washed from hide powder but when used for retanning it forms a more stable complex with chromium giving less of solubles. The soft and mellow nature of quebracho retanned leather might be attributed to this property of the tanning material. Further study with tan and non-tan fractions of the above materials with chromed and unchromed hide powder will give a further insight into the mechanism of retanning with various vegetable tan materials. Generally greater amount of washables gives rise to more water solubles as in the case of gambier where it is highest, less washables gives less of water solubles in the retan leathers as in the case of karada, goran etc.

Gambier is a mild tanning material very widely used as a mordanting agent before dyeing. But it is not suitable for retanning as it gives more of water solubles and does not produce the desired thickness also.

Quebracho, cutch and wattle give satisfactory types of retan leathers with medium amount of water solubles. It could be inferred from the series that a blend of karada or goran with myrob or divi-divi may give the same amount of water solubles as the former materials used independently. There will be an advantage by using the blend as the dark colour associated with karada or goran will be reduced. Also it will be easier in commercial practice to strengthen infusion of a bark like karada and goran to the required BK of 50° or 60° used in retanning by means of myrob extract.

The above blends for retanning have been tried on experimental pieces and the results are quite satisfactory. The process remains to be exploited commercially after successful experiment on a pilot plant scale.

T/N.T. Ratio of the tanning material used for the determinations are as follows :

Goran—2.19 ; Babul—1.08 ; Wattle—3.24 ; Karada—2.61 ; Avaram — 1.44 ; Konnam—0.79 ; Quebracho—1.62 ; Cutch—2.11 ; Myrobalan—1.32; Divi-divi—1.43 ; Gambier—0.74. When arranged in an order of decreasing T/N.T. ratio they are—

Wattle>Karada>Goran> Cutch > Quebracho > Avaram > Divi-divi > Myrobalan>Babul>Konnam>Gambier. On comparing the above series with that of increasing water solubles, there appears to be a general tendency for T/N.T. ratio to decrease with increasing water solubles of retan leather, though not in the same order.

When the question is to use retannage for army upper leathers from Indian cowhides, the percentage increase in thickness produced is of paramount importance. From the comparative study made, the following are the percentage increase in thickness obtained using the various tanstuffs for retanning.

Tan material	Percentage increase in thickness
Quebracho	9.9
Cutch	10.4
Wattle	11.3
Babul	11.0
Avaram	6.5
Konnam	6.45
Karada	14.5
Goran	14.3
Divi-divi	9.8
Myrobalan	10.5
Gambier	2.96

Here also karada and goran top the list followed by wattle, babul, myrobalan, cutch, quebracho, divi-divi, avaram, konnam and gambier in the decreasing order. The above values are not absolute and a greater concentration can give higher increase in thickness and the increase will be more predominant in loose portions of belly and shoulder.

In conclusion, it can be recommended that apart from wattle and quebracho indigenous tan stuffs like cutch, karada and goran may be used for retanning to produce leather of our choice. Further research is essential to use myrobalan and divi-divi either alone or in blends for retanning.

Discussion

Lt. Col. C. N. Hussain (*Defence Department, Govt. of India*) *:* I would like to know how the life of army boots prepared with chrome retanned leather compares with that from straight chrome leather.

Mr. S. P. Singaram : While the leather is satisfactory regarding thickness, there is slight decrease in tensile strength ; the latter is however not detrimental. The test reports are awaited.

Lt. Col. C. N. Hussain : Quantitatively, what was the decrease in tensile strength if, say, the thickness was 2.0 m.m.

Mr. S. P. Singaram : Replied he could not answer ; the author was absent.

Dr. S. K. Barat (*C.L.R.I.*) *:* For comparative studies the depth of penetration of vegetable tannin would be taken into consideration. Of course there are some physical properties like abrasion and wear resistances which depend upon the water solubles. So to assess the physical properties both chrome and vegetable tanned leathers had to be taken and the results related with particular reference to the depth of penetration.

Dr. N. Ramanathan (C.L.R.I.) : A paper on the physical properties of chrome retanned leather will be read at to-morrow's session.

Dr. D. Ramaswamy (C.L.R.I.) : Were totannins (ligno sulphonates) tried in the chrome retan studies ?

Mr. Singaram : No.

Mr. N. Viswanathan (Chemicolour Ltd., Calcutta) : Has the neutralisation aspect been studied ?

Mr. Singaram : Sodium bicarbonate and acetate are better.

Mr. Sushil Sirkar (Indian Leather Technologists' Association, Calcutta) : On what basis is the claim made by the Central Leather Research Institute that good leathers are prepared from bad hides ?

Mr. Singaram : By chrome retanning a thicker and a tight grained leather is obtained.

Dr. S. K. Barat : I want to know from Lt. Col. Hussain, as to why a thickness of 2.0 m.m. is specified. Actually in the U.S.A. there is a tendency to switch back to chrome tanned leather of less thickness.

Lt. Col. Hussain : Our experience has been that the army boots made from leather of the prescribed specifications protect the soldiers well and equip them to do their job better.

Mr. Chari (National Tannery) : As one who had been associated with making of boots for police and defence forces, my experience showed conclusively that army boots leather should have a thickness of not less than 2.0 m.m. as otherwise the soldiers would be uncomfortable and be subject to pain and fatigue while marching.

Mr. J. Ghosh (Small Industries Service Institute, Madras) : Since chrome retannage is particularly important in the Indian Leather Industry on account of the poor raw hides situation, I would like to know the cost of the chrome retannage process put forth by the Central Leather Research Institute.

Mr. S. P. Singaram : Regretted his inability to answer the question in the absence of the author.

Mr. R. Selvarangan (C.L.R.I.) : Chrome leather is stretchy while chrome retanned leather is not ; and so the life of the leather improved.

THE SURFACE CHARGE OF CHROME TANNED LEATHER AND THE EFFECT OF ORGANIC ACIDS ON IT

BY

S. GHOSH
(Central Leather Research Institute, Madras)

ABSTRACT

The surface charge and the isoelectric point of chrome tanned leathers have been determined electro-osmotically using samples tanned with anionic and cationic chrome as well as those of basic chromium sulphate tanned leather treated with oxalic, citric, tartaric and lactic acid solutions separately. It has been shown that while cationic chromium raises the isoelectric point of hide, anionic chromium lowers it ; the treatment of cationic chromium tanned leather with any complex forming organic acid also lowers the isoelectric point. The importance of these findings has been discussed in the light of tannery experience.

It is common practice in modern tanneries to adjust at every step of the manufacture of leather, the pH of the liquor. The real importance of the pH will however be understood if we remember that the hide substance, being an amphoteric protein will have different surface charge depending on the pH of the medium and it is this surface charge that determines to a large extent the reaction of the hide with the other ionic substances in the liquor. Thus, the penetration and fixation of tans will depend on the charge of the hide protein while the subsequent fixation of dye or fat-liquor, on the surface charge of the tanned hide.

The techniques[1,2,5] hitherto employed for determining the surface charge of hide or leather materials, are either indirect or require the material in a powdered form. A simple but direct electro-osmotic method of determining the surface charge has been developed by the present author where the hide or leather as such can be used as membrane. Determination of the surface charge and isoelectric point of hide and several leathers using this method has already been communicated.[3] Here, some further work on the determination of the surface charge of chrome tanned leathers of different types, as well as the effect of some organic acids used in masking on the surface charge of chrome tanned leather has been described.

Experimental

Delimed and bated goatskin was tanned in one-third basic chromium sulphate solution. Pieces from the freshly tanned goatskin were soaked separately in N/10 solutions of different organic acids like citric, oxalic, tartaric and lactic acids for 3 days. The soaked pieces were washed with distilled water and then the electro osmosis through each type of leather was measured using HCl or NaOH for adjusting the pH of the solution and NaCl for adjusting the conductivity. The procedure was as described in the earlier paper.[3]

In order to study the effect of anionic and cationic tannage, bated goatskin was tanned using chromi-oxalate, which is an anionic complex of chromium and separately with 1/3 basic chromium chloride, containing cationic chromium complex respectively. The methods of preparing the liquors were as followed by earlier workers[1,5]. The final concentration of chromium in both these solutions were 15 gms. Cr_2O_3 per litre ; the solutions were aged two weeks before using for tanning. After tanning the pieces were taken out, washed and neutralised by bicarbonate to pH 7 and soaked in borate buffer for electro osmotic measurements.

The results of such measurements have been shown in Figures 1 and 2 and the isoelectric points of the samples determined from these curves are given in Table I. The isoelectric point for a particular material, it may be mentioned, represents the pH at which the surface is uncharged ; below the isoelectric point the surface is positively charged and above it, it is negatively charged.

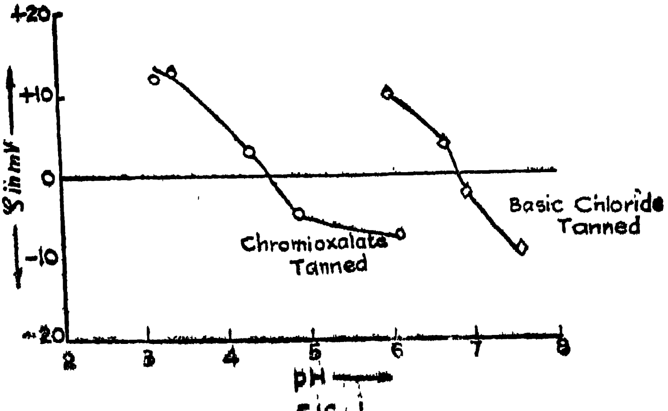

FIG. 1

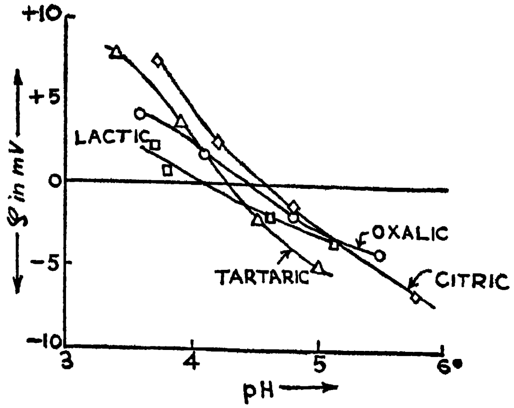

FIG. 2

TABLE I

	Treatment			Isoelectric point
1.	Chromium chloride tanned			6.7
2.	Chromi-Oxalate tanned			4.6
3.	Basic chromium sulphate tanned treated with			
	Do.	do.	oxalic acid	4.3
	Do.	do.	tartaric acid	4.3
	Do.	do.	lactic acid	4.1
	Do.	do.	citric acid	4.55

Discussion

The above results point to some important characteristics of the reaction between hide and chromium salts. Thus in accordance with the view of Gustavson[5] and Otto[6] it has been observed that cationic chromium tanned leather has a relatively high isoelectric point (IEP) whereas that tanned with anionic chrome has a relatively low IEP. It may be also concluded from the effect of the organic acids that they lower the IEP possibly by forming anionic complexes with chrome in the chrome tanned leather.

The importance of these results in the light of tannery experience is that the ordinary basic chromium sulphate tanned leather at values of pH as high as 6 will be positively charged[5,3] and will take up anionic dyes and not the basic dyes. If the pH of the system is lower so that the surface density of charge is very high there will be a too quick fixation of anionic dyes and this is not desirable for level dyeing.

Now, the masking agents and neutralising agents containing complex forming organic anions, lower the IEP (the extent of lowering depending on the amount used and the pH) and thus at values of pH 5–6 the surface density of the charge will decrease and the charge may even assume a negative sign. In the former case a levelling of anionic dyes is effected, in the latter case basic dyes are fixed. A previous application of any other colourless anion or even a weak solution of tannin makes the surface less positively charged. The 'Tamol' brand of mordants also makes the basic dyeing of chrome-tanned leather possible by decreasing the positive charge.

It must be mentioned that during drying also the cationic chara basic-chromium sulphate tanned leather decreases, and the uptake of is made more difficult.

The same is true in case the leather is fat-liquored prior to dyeing anionic fat-liquor. In case the charge condition is desired to be kept unc as in the case of the production of velvet leather, fat-liquors using e as emulsifier may be used.

It must be mentioned that if the positive character is less pronou absent, there will be more penetration of the cationic dyestuff or fat- For fixation, however the charge condition must be such that the surf a pronounced opposite charge. In dyeing with anionic dyestuffs, as su by Otto[6], it may be sometimes better first to allow the dye to penetrate desired extent, and then use some cation active compound for fixation.

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PLEA FOR TREATMENT OF DYEING AND TANNING SUBSTA ON THE SAME BASIS AS WATTLE EXTRACT AND WATTLE B

BY

P. V. VITTAL RAO

(*A.V. Thomas & Co., (India) Ltd., Madras*)

ABSTRACT

Syntans are now recognised to be important auxiliaries in the production of better l being available in various ranges. Hence it is urged that the Government should c these also as tanning materials along with wattle bark and wattle extract and extend import concessions.

The tanning industry has advanced rapidly during the last 20 years. may say that the two world wars helped it to grow to a great extent. E.I. Kips produced by our tanners were purchased by the then His Ma Government, which encouraged tanners to produce more by giving them benefits.

Along with the production of leather, the methods of tanning also to develop, and tanners began to show interest in finding out various vegetable tanning materials and auxiliaries to produce better leather a cost and in the shortest time. As in the initial stages only wattle bar wattle extract were imported, the Government classified these two ite Part IV of the I.T.C. schedules. But dyeing and tanning materials classified separately under Section V. Perhaps the Government then di think that synthetic tanning materials would be much in demand.

We may as well remember that even wattle did not receive any encou ment in the initial stages. Tanners who were using avaram and konnam did not feel using wattle as worth while and importers of prime quality v bark and wattle extract found it very difficult to induce tanners to try for a change. Once tanners recognised in wattle a superior vegetable tanning material, demand for it began to grow. But the ban imposed by Government on South African Import trade created a problem There was good demand but supplies were limited, as we had to get them only from East Africa. When wattle was not available, tanners tried various other substitutes like quebracho, chestnut, valonia, etc., but always found that the colour that they obtained was not the same which they used to get from wattle.

With the development of leather chemistry and improvements in the techniques of tanning, syntans began to be recognised as an important auxiliary for production of better leather. Factories in Germany, France, U.K., U.S.A. and other countries have produced various ranges in syntans for almost all the needs of tanning such as bleaching, weight-giving, quick-penetration, filling, sludge-dissolving, cutting of tanning period etc.

By now syntans have established a claim for their being considered as an important raw material like wattle extract and wattle bark. But as they are under separate classification, the concession importers are getting for importing wattle extract and wattle bark is not available for import of syntans. It is perhaps due to lack of representation to the Government. It is well realised by tanners and those connected with the leather trade that syntans as leather auxiliaries are necessary to produce better leather and shorten the period of tanning with economy in cost of production. Syntans cannot entirely replace vegetable tanning materials and to the extent syntans are used, that quantity of pure tannin can be saved. Hence the tanner gets extra benefits in improving the quality of his leather by use of syntans.

Some of the syntans developed in foreign countries have proved to have remarkable properties and by their incorporation our tanners could get much better finish and produce better class of leather. When the import policy was recently modified and OGL abolished, special concessions were given to the import of wattle extract and wattle bark. The Government were able to appreciate the importance of the Leather Industry and the foreign exchange it was earning for our country. But tanners were hard-put to obtain their requirements of syntans as the same concession was not applicable to the import of syntans.

Everyone realises that for our country to pass over the difficult period, exports should be stepped-up to the maximum. Of the major foreign exchange earners, leather is one and it is but reasonable to expect our Government to assist the tanners by making available to them the raw materials that are necessary for producing better leather at less cost. After all, the total import of syntans would only be about 10% of the total quantity of tanning materials necessary and this would not affect the foreign exchange position if import of syntans and leather auxiliaries are allowed to be imported under wattle extract and wattle bark licences.

The import of raw materials for industries should be based on the requirements of a particular Industry It will not be far when we will be self-sufficient in our requirements of syntans and other vegetable tanning materials. But till then we have to see that our Tanning Industry is not hampered in its advancement by lack of necessary raw materials. When plastic, glass and other industries are encouraged to get their raw materials, Leather Industry should not be left alone. Considering all the above points, it is submitted that—

1. Synthetic tanning materials and leather auxiliaries should be considered tanning materials along with wattle extract and wattle bark.

2. There should be one single classification in the I.T.C. Schedule "Tanning Materials," which will allow import of wattle extract, wattle bark, synthetic tanning materials and leather auxiliaries.
3. Holders of import licences for wattle extract and wattle bark should be allowed to import syntans and leather auxiliaries under their licences for wattle bark and extract.

Chairman's concluding remarks

Winding up the proceedings, the Chairman said that while the paper on aluminium salts was interesting, further experiments were necessary before conclusions could be drawn. Decision as to whether a particular type of leather was good or bad should be from the consumers' point of view. If the author of the paper on syntans had given a lay-out for producing these from indigenous materials, he would have been happy. At present, it is only the Indian tanneries which have specialised in use of syntans that could utilise syntans. The E.I. Tanning Industry was of late utilising them as bleaching agents. Manufacture of syntans from indigenous materials would decrease, if not end, imports. Mr. Vittal Rao's paper actually should have been addressed to the Development Wing (Leather), of the Ministry of Industry and Commerce.

As regards chrome retanning, the Chairman said that vegetable tannin had come to stay as a retanning agent. There were difficulties like crackiness during glazing (though this disappeared on hot plating). The papers on hexamethylene tetramine and on chromatographic studies were interesting; but they might not be of much use to the tanner.

The Chairman would not agree that good leather could be ever made out of bad hide; only saleable leather could be obtained. The position of the research chemist in relation to the tanner was that of a physician to the patient. The research chemist should go to the tanner, watch the processes at each stage, formulate and demonstrate on the spot the profitable processes evolved by intensive and elaborate researches. He should convince the tanner. The tanners and the Government departments had a common objective in regard to plans and development programmes for the country. To achieve this, it was necessary the teams of research workers should go out to the various tanning centres and stay there for some months if fruitful results were to be achieved. It was very difficult for the Indian Tanning Industry to depend solely on non-hydrolysable tanning agents. He would suggest that the possibility of introducing condensible properties to hydrolysable tannins like myrobalans, be studied so that these might be better utilised.

Dr. D. Ramaswamy proposed a vote of thanks.

PROCEEDINGS OF THE TECHNICAL SESSION III

(*Sunday, the* 16*th March,* 1958 *Forenoon*)

Chairman : Mr. Vasant Pandit, Western India Tanneries, Bombay.

Recorder : Dr. E. C. Mathew.

Dr. S. K. Barat introduced the Chairman.

After initiation of the Session, the following papers were read in the order indicated below :—

Potentiality for the manufacture of and use of tannin extracts from indigenous tanning materials	Read by Mr. R. Selvarangan.
Problems confronting tannin extracts manufacturers in India	Read by Mr. J. K. Kothari.
Babul bark and possibilities of its extract manufacture	Read by Dr. V. S. Padmanabhan.
Evaluation of the properties of natural tannins by means of fractional tanning	Read by Prof. A. N. Mikhailov.
Production of extracts ...	Read by Mr. Leitensdorfer.
Need to change over to vegetable tannin extracts	Presented by Dr. E. C. Mathew.
Rapid sole leather tannage ...	Taken as read.
Rot resistance in sole leathers—Some recent developments in South Africa	Taken as read.
Impregnation of sole leather ...	Read by Mr. J. Budaga Rao.
New tanning materials ...	Read by Mr. M. K. Udaya Varma.
Some theoretical considerations pertaining to the modification of lignin sulphonates for tanning purposes	Read by Mr. K. B. Mathur.
Assessment of tanning potentiality of some modified ligno sulphonates.	Presented by Dr. S. K. Barat.
Flavogallol—Constituent of the tannin from pomegranate rind	Taken as read.
A survey of indigenous tanning materials	

POTENTIALITY FOR THE MANUFACTURE OF AND USE OF TANNIN EXTRACTS FROM INDIGENOUS TANNING MATERIALS

BY

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ABSTRACT

The production, consumption and potential demand for tannin extracts in India, the characteristics of indigenous tanning materials and their availability, the possibilities for the manufacture of tannin extracts individually or in blends or by suitable chemical modifications for various uses are discussed.

Tannin and its uses

Tanniferous plant species are found all over the world. Whether they are put to use or not depends entirely on (i) the size of the country, (ii) the tannin content of the plants, (iii) the properties of the particular tannin and (iv) its price at the place of consumption. The tannins are used in the tanning industry in the form of either the raw tanning material or tannin extracts. The latter are richer in tannin content and prepared by leaching the tanning material (wood, barks, fruits, pods, nuts, leaves and roots) and concentrating the liquor thus obtained to a liquid, solid or powder form.

Tannin extracts are chiefly used for tanning in straight and combination tannages. They are also used in making boiler compounds, in conditioning mud in well drilling, as mordant in dyeing, in preserving fishing nets, as derusting agent, as antioxidant, in making resins and adhesives, in making inks, in medical preparations and in many other ways.

World production of tannin extracts and consumption

The world production of tannin extract is estimated at 500,000 tons per annum. The following figures for the production of various tannin extracts are based on the import and export figures of extract manufacturing and consuming countries.[1] (Table No. I)

TABLE I

World production of the various tannin extracts

Extract	(000) tons
Quebracho extract ...	175
Chestnut extract	150
Mimosa extract	115
Myrob extract	12*
Other extracts (sumac, valonia, myrtan and blend extracts)	12
Total ...	464

The United States and U.K. depend on imported tanning materials. The U.S. imports about 90,000 tons of vegetable tannin extract for local consumption and 23,000 tons of tanning material for the manufacture of blend extracts. U.K. imports about 55,000 tons of various extracts for local consumption and 21,000 tons of myrobalan from India for the manufacture of tannin extract. India imports about 7000 tons of mimosa extract and 7000 tons of wattle bark worth 10 million rupees annually.

Potential demand for the tannin extract in India

22 crores worth of E.I. tanned skins and kips tanned by vegetable tanning materials are exported annually. Sole leather is mainly produced by vegetable tanning. Even chrome tanned leather is nowadays, retanned with vegetable tannins. Vegetable tanning also finds a place in the manufacture of various types of leathers like belting leather, harness, upholstery, picking band etc. Although numerous synthetic tannins are marketed, they cannot be used as substitutes for vegetable tannins. They are used as auxiliaries and for special tannages. Further these synthetic tannins are more expensive. Thus it is clear that the tanning industry in India depends mainly on the vegetable tannins.

The potential demand for the tannin extract in the Indian Leather Industry is roughly calculated to be 60–70,000 tons, from the annual production of hides and skins in India.[2] (Table No. II)

TABLE II

Potential demand for the tannin extract by the Indian leather industry

	Annual production in millions 1952	Average weight of a delimed hide or skin (in lbs.)	Percentage of total production of vegetable tanning	Percentage of tannin extract required on delimed weight	Potential demand of tannin extract in tons
Cow hides	15.9	20	50	30	21.250
			40*	10	5,679
Buffalo hides... ...	5.2	35	75	50	30,395
Sheep skin	15.5	3	80	25	4,151
Goat skin	21.3	4	70	25	6,656
				Total	68,231

* Vegetable combination tannages.

Tanning extract industry in India

Myrobalan extract has been prepared in India for over 30 years and it is the only tannin extract, the manufacture of which has so far proved a success in India in spite of the various adverse circumstances under which it has to thrive. India produces approximately one lakh ton of myrobalan nuts per annum, out of which the three tannin extract factories at (1) Kharagpur (2) Raniganj and (3) Amba consume about 10,000 tons and produce 4000 tons myrobalan tannin extract in solid and powder form ; the major portion of it (3,500 tons) is exported to U.K. The myrobalan extract manufactured in India is not favoured by the Indian tanners, in general, as a substitute for myrobalan nuts. However, the bleached myrobalan extract powder[17] recently manufactured by Shree Lakshmi Tannin Extract factory, Kharagpur with technical assistance from Central Leather Research Institute can be used in the place of myrobalan nuts. Cutch extract is also made in India but the quantity is small and the cost too high to permit its regular use in leather industry.

Scope for use of extracts in India

Indian requirements in vegetable tanning are mainly met by the indigenous tanning materials like avaram, babul and myrobalan, supplemented by imports of mimosa extract and wattle bark. Myrobalan-nut or extract—is not used alone in vegetable tannage and hence the production of some other suitable tannin extract is necessary if India is to be self-sufficient in extracts.

The demand for tannin extract is ever growing due to the noticeable increase in the use of extract in the place of tanning materials and the newer uses to which they are being put. The Indian Railway is interested in using tannins in boiler compound and as a derusting agent. The oil companies in India can use considerable amount of tannin in making drilling mud mixture. 500 to 1000 tons of drilling mud chemicals are used in drilling a typical oil well. India can also use tannin extensively in making resin, adhesives, inks and dyes and medicines etc. Hence it is high time that India should be made self-sufficient and also an exporting country in the tannin extract by proper collection and utilization of the various indigenous tanning materials.

The availability of indigenous tanning materials for the manufacture of tannin extract

For manufacturing tannin extract, the tanning material must be cheap, rich in tannin and available in steady and plentiful supply. Scientific research plays an important part in the manufacture of extracts through determining the optimum conditions for leaching, lightening the colour of the tan liquor, and arresting the fermentation of tannin infusion[16] and in determining use as a substitute for a known tanning material through chemical modification or proper blending. Such studies have been made at the Central Leather Research Institute.

The supply of wattle work from indigenous sources is still inadequate. Extensive wattle plantation has been started in the Nilgris and Upper Palnis and other places in an area of 22,000 acres to yield annually about 11,000 tons of wattle bark on 10 years rotation. At present 4000 tons of bark are supplied every year. Nursery and small scale field tests are being carried out in Assam, Bombay, Orissa, Punjab, Uttar Pradesh and West Bengal for locating suitable areas for the plantation of wattle trees.[4,5] The eucalyptus species such as those already used for production of tannin extract in Australia, and others such as 'Malleto' and Redunca[1] 'Myrtan' and other eucalyptus species, such as Sideroxylon may be tested here for plantation. 'Myrtan' is a mixture of catechol and pyrogallol tans and is closely akin in action to French and Italian chestnut[6,7]. Further proper care of the tanniferous trees and protection against felling them for fuel have to be incessantly taken.

Various tanning materials, reported to be good tanning materials alone and in combination by various research workers[8, 14] and their availability in India are given in the following Table (Table III). Information, obtained recently from various states are also included in the Table.

TABLE III

No.	Name of species	Distribution*	Average tannin content	T/NT
			(Percent)	
1.	Myrobalan (*Terminalia chebula*) nuts.	Practically all States, especially M.P. (35,000, Bombay (9000), Bihar, Andhra and Madras.	30	2.3
2.	Divi-divi (*Casealpinia coriaria*) pods	Madras and Andhra.	33	1.2
3.	Dhawa (*Anoegeissus latifolia*) leaves	Punjab, U.P. (500), Rajasthan, Bihar, M.P., Bombay, Mysore, Coorg (8) Kerala, Madras and Andhra.	20	1.5
4.	Wattle (*Acasia mollissima*) bark	Madras.	35	3.0
5.	Mangrove (*Ceriops roxburghiana*) bark and other mangrove species	Andamans, W. Bengal (366) Orissa, Kerala, Bombay and Mysore	27	4.0
6.	Hopea (*Hopea parviflora*) bark	Mysore, Kerala and Madras.	21	4.0
7.	Kodukkapuli (*Pithecolobium dulce*) bark	Cultivated as hedge plant throughout greater part of India.	34	3.6
8.	Karada (*Cleistanthus collinus*) bark	U.P., Orissa, Bihar, M.P., Mysore, Madras, Andhra, Bombay	30	2.5
9.	Kahua (*Terminalia arjuna*) bark	M.P., U.P., (20) Bihar, Orissa, Andhra, Kollegal (4), Madras, Andamans.	23	2.0
10.	Casuarina (*C. equistifolia*) bark	North Kanara, Nellore, Bombay, Bengal and Andamans.	10	3.6
11.	Babul (*Acacia arabica*) bark	Punjab, U.P. (655), Rajasthan, Bihar, M. P., Bombay, Madras and Andhra.	15	1.5
12.	Eyal vagai (*Peltophorumferrugineum*) bark	Andamans and Madras	20	2.1
13.	Vagai (*Cassia marginata*) Bark	Madras and Travancore	15	2.1
14.	Avaram (*Cassia auriculatu*) bark	Mysore, Madras (1000) Andhra and Bombay	18	1.7
15.	Konnam (*Cassia fistula*) bark	Madras, Orissa and C.P.	10	0.8
16.	Vel Velam (*Acacia leucophloea*) bark	Punjab, U.P., Rajasthan, M.P., Bombay, Mysore, Madras and Andhra.	17	2.4

*Figures given in brackets are the amount of tanning materials in tons reported to be available in the respective states.

Physico-Chemical characteristics of the various tanning materials and their uses in tanning

Myrobalan, Divi-divi and Dhawa are of pyrogallol type. Myrobalan contains considerable amount of weak acids and is used for topping and bleaching the catechol tannin tanned leather. It can also be used, in tanning, blended with catechol tannins. Divi-divi and Dhawa can be used in the place of myrobalan in certain cases. Wattle is a catechol tannin and fairly astringent and contains less of weak acids and salts. The physico-chemical characteristics are similar to those of other catechol tannin—like Mangrove, Karada, Hopea, Kodukkapuli and Casuarina and the mixed tannin Arjuna for tanning purposes. These can be used in light leather tannages in blend with avaram and babul and in heavy leather tannages, alone and in combination with pyrogallol tannins (*e.g.*, myrobalan). Babul is a catechol tannin and less astringent. It contains less of acids and more of salts. The catechol tannins like vagai and Eyal vagai can be used in its place. Avaram is a mild catechol tannin. It contains more of salts and appreciably buffered Konnam and Vel Velam can be used in its place.

Experimental production of various straight and blend extracts

These tanning materials can be used in the manufacture of straight tannin extracts. Various blended tannin extracts can be prepared with knowledge about the physico-chemical characteristics of the tanning materials and their uses in tanning.

West Bengal is reported to be working on a scheme to utilize the goran bark available locally for the manufacture of tannin extract. Central Leather Research Institute is in contact with various institutions, Directorate of forests and tannin extract factories to assess the availability of the various indigenous tanning materials and utilize them in the preparation of tannin extracts. Various straight and blended tannin extracts were prepared on a small scale using a battery system of leaching and spray drying the leached tan liquor. The results of analysis of the extracts of the preliminary experiment and their suitability for tanning are given in Table IV. The analytical data given in the Table are tentative since these extracts can be improved on further experiments and on large scale production.

The tannins used in various blends are given below :

1.	E.I. Tan M.A. 7	Wattle and Avaram
2.	E.I. tan M.A.B. 11	Wattle, Avaram and Babul
3.	Sole tan T.C. 3	Myrobalan, Cutch and Extract
4.	Sole tan T.B. 3	Myrobalan and Babul
5.	Kip tan ABK	Avaram, Babul and Karada
6.	Sole tan BKD	Babul, Karada and Divi-divi
7.	Sole tan DCTM	Sole tan BKD, Myrob extract and Cutch Extract.

TABLE IV

No.	Tannin extract	Percentage				T/NT Ratio	Analytical solution				Weak acids	Salts of weak acids	Total weak acids and salts	Uses in
		Tannin	Non-tannin	Insols	Moisture		Colour			pH				
							Y	R	B					
											(100 gm./m. eq.)			
1	Mimosa ...	68.65	25.12	2.64	3.59	2.74	20	10	0.7	4.7	10.88	33.96	44.64	E.I. and heavy leather tanning.
2	Karada ...	65.15	23.82	2.87	8.16	2.70	20	11	0.1	5.0	3.92	50.96	54.88	E.I. and heavy leather tanning and as a substitute for wattle.
3	Eyal Vagai.	59.00	31.25	5.25	4.5	1.90	9	4	...	3.8	18.8	51.8	70.6	E.T. Tanning and as a substitute for wattle.
4	E.I. Tan MAB 11.	55.03	36.88	2.84	6.25	1.48	25	7.1	0.1	4.8	21.76	54.20	75.96	E.I. tanning.
5	Soletan TC 3	46.0	39.25	8.0	6.75	1.18	40	11	0.1	3.4	57.2	22.80	80.00	Sole leather tanning.
6	E.I. Tan MA7.	60.73	30.87	3.41	4.99	4.96	20	10	0.1	5.3	10.88	73.40	84.28	E.I. tanning.
7	Avaram ...	54.92	32.60	3.13	9.35	1.71	40	10.5	...	5.3	13.04	87.4	100.44	E.I. and Kip tanning.
8	Soletan TB3	48.08	40.57	7.77	3 58	1.19	10	3	...	3.7	80.40	38.60	119.00	Sole leather tanning and bag tannage.
9	Divi-Divi ...	49.93	37.69	8.23	4.15	1.33	9	2	...	3.7	108.0	40.0	148.0	Heavy leather tanning.
10	Kiptan ABK	52.5	40.7	2.4	4.4	1.29	15	5	...	4.4	57.2	98.64	155.84	Kip tanning.
11	Konnan ...	29.80	56.6	6.0	7.6	0.53	12	20	0.2	5.4	13.0	146.6	159.6	E.I. tanning.
12	Soletan BKD	34.2	57.1	2.5	6.2	0.60	8	2.5	...	3.7	130.32	54.20	184.52	Kip and heavy leather tanning.
13	Myrob ...	64.2	28.5	2.6	4.7	2.25	3	0.5	...	3.3	180.0	34.96	214.96	Myrobing and in blends.
14	Soletan DCTM	42.2	49.5	2.6	5.7	0.85	14	3.2	...	3.7	186.80	78.68	265.48	Heavy leather and kip tanning.

The tannin extracts prepared may be arranged in series as follows :

1. *In the order of decreasing tannin content :*

Mimosa>Karada>Myrob>E.I. Tan MA7>Eyal Vagai>Avaram> E.I. Tan MAB 11>Kip Tan ABK>Divi divi>Soletan TB3>Soletan TC3> Soletan DCTM>Soletan BKD>Konnam ;

2. *In the order of decreasing T/NT value :*

Mimosa>Karada>Myrob> E.I. tan MA7>Eyal Vagai>E.I. tan MAB11 >Avaram >Divi-divi>Kiptan ABK>Soletan TB3>Soletan TC3>Soletan DCTM>Soletan BKD>Konnam.

3. *In the order of decreasing acidity :*

Soletan DCTM>Myrob>Soletan BKD>Divi-divi>Soletan TB3> Soletan TC3>Kiptan ABK>E.I. tan MAB 11>Eyal vagai> Avaram> Konnam>E.I. tan MA7>Mimosa>Karada.

4. *In the order of decreasing content of salts of weak acids :*

Konnam>Kiptan ABK>Avaram>Soletan DCTM>E.I. tan MA7> Soletan BKD>Divi-divi>E.I. tan MAB11>Karada>Eyal Vagai>Soletan TB3>Myrob>Mimosa>Soletan TC3.

5. *In the order of decreasing buffering action of the tanliquor :*

Soletan DCTM>Myrob>Soletan BKD>Konnam>Kiptan ABK> Divi-divi>Soletan TB3>Avaram>E.I. tan MA7>Soletan TC3>E.I. tan MAB11>Eyal Vagai>Karada>Mimosa.

6. *In the order of decrease in pH of the tan liquor :*

Konnam>Avaram = E.I. tan MA7>Karada>E.I. tan MAB11>Mimosa >Kiptan ABK>Eyal Vagai>Soletan TB3 = Divi-divi = Soletan TB3 = Soletan DCTM>Soletan BKD>Soletan TC3>Myrob.

7. *In the order of decreasing lightness of the colour imparted to the leather by the tanliquor :*

Myrob>Konnam>Soletan TB3>Mimosa>Karada>E.I. tan MA7> E.I. tan MAB11>Avaram>Eyalvagai>Kiptan ABK>Soletan TC3> Soletan TB3>Soletan DCTM>Soletan BKD>Divi-divi.

Besides, the list of the straight and blended extracts given above, various other extracts can also be prepared. Straight extracts can be prepared from Hopea, Arjuna and mangrove and also in blend with myrob or dhawa for tanning and other purposes. A modified Divi-divi extract[16] can be prepared from Divi-divi pods, for use in sole leather tannage. A systematic study on Indian Myrobalan may lead to the production of extract, similar to sweetened chestnut extract which is used in the place of mimosa. The inherent undesirable characteristics of the abundantly available tanning materials may be remedied by proper blending and modifications.

The ratio of weak acids to salts of weak acids in the tan liquor can be adjusted by the addition of acid or alkali. The buffering action of a tan liquor may also be increased by the addition of known weak acids and salts of weak acids. Highly buffered tan solution may be made less buffered by passing through suitable ion exchange resins. The colour of the tan liquor can be improved by chemical and physical treatment and its pH can be adjusted to the desired extent. The solubility of the extract can be increased by sulphitation. The variations which can be effected by the treatment mentioned above can also be obtained by proper blending of the various tannin extract and by combination of battery and successive leaching.[15] Thus the tannin extract suitable for the manufacture of a particular type of leather can be prepared by proper blending and treatment of the indigenous tanning materials.

Extensive plantation of tanniferous trees, proper collection of the promising indigenous tanning materials, manufacture of tannin extracts (straight, blend and modified) and expanding and exploring the uses of tannin extracts in tanning and other purposes will undoubtedly go a long way in stabilising the tannin extract industry and increasing the potential demand for the tannin extract in India.

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PROBLEMS CONFRONTING TANNIN EXTRACT MANUFACTURERS IN INDIA

BY

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ABSTRACT

Myrobalan, though it is a monopoly of India, is very largely exported to foreign countries, some of which are manufacturing extract out of it and making huge profits whereas in India, manufacturers of myrobalan exctract are encountering many handicaps as a result of which factories cannot be run to their full capacities and their margin of profit is very small. Some of the handicaps are the forest legislations and restrictions in railway transport, hampering the collection and transport of myrobalan nuts, and imposition of inadequate duties on raw myrobalans to counter-balance the free import of it in foreign countries, rigid labour legislations and lack of assistance from Trade Commissioners in foreign countries to popularise our product.

It is really a pleasure and privilege to appear before this august assembly and to discuss problems facing the manufacturers of tannin extracts. Not being a technician, the author does not venture to discuss the technical matters connected with the industry. Only the business side of the industry and the difficulties experienced in the manufacture, marketing, transport, etc., of Myrobalan extract will be dealt with on behalf of the Myrobalan Extract Manufacturers' Association.

In the course of the last 25 years, we have had many vicissitudes and as is common with any new industry for which there is no market at home; we had to face competition from highly industrialised countries of the West. There are at present in India, three factories manufacturing solid myrobalan extract. They are :—(1) Shree Laxmi Tannin Extract Factory at Kharagpur (West Bengal) owned by Purshotam Mathradas & Co. Private Ltd., Bombay. (2) Amba Factory at Amba Vishalgadha near Kolhapur, owned by Amba Tannin and Pharmaceuticals Ltd., Bombay and (3) Raniganj Factory (West Bengal) owned by New India Tannins Ltd., Calcutta. Out of these three, the Laxmi Tannin Extract Factory, Kharagpur, is producing spray dried powder also for the last 10 years. It may be of interest to know that this factory has set up another spray drier plant in August, 1957, which except for the atomizer, has been entirely fabricated in the factory itself, thereby saving vital foreign exchange. All these three factories depend upon foreign markets and in the past there was competition among them. Happily now, these three factories have joined together to form an association and have thus saved themselves from competing among themselves. There is of course a healthy competition among them in trying jointly to manufacture superior quality extracts and to compete successfully with foreign manufacturers. Due to lack of technical knowledge, the efficiency aimed at, has not yet been realised. (But it is gratifying to state that the Central Leather Research Institute is helping us to overcome some of our difficulties).

Our country though rich in natural resources needed for industrial development, needs technical training, guidance and co-operation from the Government Departments concerned. Since it is not possible for a small industry like ours to be fully informed about the technical developments taking place in other countries, our embassies in other countries could observe new technical developments there and keep the industry here well informed about the same.

Myrobalan is the monopoly of this country and its importance does not need emphasis. Myrobalan is grown in the forest area of States like Madhya

Pradesh, Orissa, Bombay and West Bengal. Since myrobalan is an important forest produce, the concerned State Governments should see that the trees are well-preserved and carefully looked after. Actually, myrobalan trade is adversely affected by the wrong procedures followed by the forest departments. Formerly, the forests were sold by public auctions and fetched good price. Nowadays however, there are no bidders for the same. This loss of large revenue is viewed with concern by the Government, who, however, have not been able to set right this state of affairs. Under the existing rules and procedures, much theft from the forest areas occurs.

Myrobalan collection could be an additional source of income to the forest tribes and villagers, to augment their earnings, during the agricultural season. Propaganda amongst the villagers is necessary to provide impetus for collecting myrobalans from the forest. Formerly, the contractors used to do this propaganda ; now in the absence of such propaganda collection is much reduced.

The movement of myrobalan from the forests to port of shipment or to the factories by rail is an important factor for the trade. There is a lot of uncertainty relating to this movement and this has affected the trade and the industry very badly, for the raw materials cannot reach the factories in time and this results in closure of the factories for considerable time. This delay in transport results in deterioration of the goods also. Myrobalan extract is mainly exported. Due to inordinate delays in executing orders, much business is lost. So Government must do something to overcome these difficulties. Another way in which transport problems affect the trade is as follows : During the winter months the whole supply is hard hit due to insufficient availability of empty wagons ; the winter months form the best part of the year, especially, for production of spray dried powder.

In spite of myroabalan being a monopoly of this country, foreign buyers are exploiting the situation in the absence of any organisation of trade and proper control by the Government. The Indian Railways have been importing large quantities of foreign extracts for treatment of water fed to the boilers. It is a known fact that myrobalan extract is a suitable substitute for the chestnut extract which is imported at double the cost. So, adoption of use of the indigenous myrobalan extract would not only save money but also help the local industry. Government should come forward to help this industry in these ways and it is requested that the sponsors of the Symposium will represent these facts to the Government. Further, propaganda amongst the tanners is necessary to popularise myrobalan extract and to bring out the advantage of this indigenous product in preference to imported extracts. It gives satisfaction to learn that Central Leather Research Institute and the Forest Research Institute at Dehra Dun, are making efforts in this direction.

As regards labour laws, these small industries should not be treated at par with other well-developed industries. An industry can flourish only with full co-operation between the management and labour. The various Acts and Regulations are for achieving this. Unfortunately in the majority of cases, it does not happen so. Labour disputes result in lot of time, money and energy being wasted and they divert the attention of the management. Sometimes the situation gets out of control and involves lives of personnel and the management. So if the production is to be increased and industries are to be well settled and established, necessary steps in this direction will have to be taken.

Under these circumstances, it is felt that the Government should appoint a Committee to look into the problems of small industries like ours and recommend the steps to be taken. While the problems are many, the following require serious consideration :

Proper legislation for collection of myrobalans in the forest, transport facilities, suitable steps to counteract the duty-free import of raw materials into other countries, and help and co-operation from foreign embassies through supplying technical information and finding suitable markets for the products.

Discussion

Dr. A. Seetharamiah, (Development Wing (Leather), Ministry of Industries and Commerce, Government of India) : There are three main problems facing the myrobalan extract manufacturing industry, (i) facilities by railways for transporting myrobalans from forests, (ii) preferential freight rate charged by foreign shipping companies in transport of myrobalans and (iii) heavy duty on myrobalan extracts by the importing countries.

The problem regarding transport by rail was common to other industries also. The Railway Board is evolving a policy for maximum utilisation of the carrying capacity of the wagons. The second problem is receiving the attention of the Government. As regards the third the Government of India had entered into trade agreements with countries like Poland, Rumania, etc., and so there were prospects for increasing exports of myrobalan extract. The suggestion to put an export duty of raw myrobalans is not a sound one. While the Government of India is giving careful consideration to all the problems, it is not the Government alone that could take a decision.

Dr. Y. Nayudamma : As. Dr. Seetharamiah has put it, the problem is to be viewed not from manufacturers' point of view only, but from other angles also. The views expressed by Mr. Kothari could be put through the Leather Export Promotion Council, which is meant for leather auxiliaries also.

The Railways are using at present 7–8 thousand tons of imported extract for treating boiler feed waters, etc. Could Myrobalan extract be used instead?

Mr. Leitensdorfer : The Railway Board tells that it is quite impossible to use an extract other than quebracho.

Dr. S. K. Barat (C.L.R.I.) : The Railway Board is now thinking of changing over to the use of cutch extract with some modifications. So far as the myrobalan extract is concerned, the Railway Board is convinced that it is not suitable as it has a corroding effect.

Dr. Y. Nayudamma : Myrobalan extract could be used if it could be suitably modified. Prices of cutch extract have gone up very high recently.

Mr. Bhagwat (Modern Tanneries) : A mixture of cutch and soda ash is found useful.

BABUL BARK AND POSSIBILITIES OF ITS EXTRACT MANUFACTURE :

BY

Kapurthala Northern India Tanneries Ltd.

ABSTRACT

The article brings out the utility of babul bark for making into extract. The author reports to have used babul bark and produced sole leather comparable with English sole leather. Babul bark is used along with myrob in tanning. If babul extract is made, leach houses in the Indian tanneries will be empty as they are in Europe and more of myrobalam used in tanning would be processed extract. Babul extract may also be suitably modified as done in the case of chestnut and mimosa extracts.

Introduction

Babul bark constitutes the most important tanning material of Northern India. The consumption of bark in Kanpur alone is over 5,00,000 maunds per annum. Babul bark is generally used along with myrob. While myrob extract is manufactured in India, babul extract is not being made at present. However, an attempt made to manufacture it, came to an end due to the depression of 1930's. Babul bark has been adjudged a good tanning material both by the leather chemist and the practical tanner.

Properties

Rottsieper[1] classifies, babul bark as " Mixed Tannin." In the literature, it is generally referred to as " Catechol Tannin." Burton and Barat[2] state that its concentration of weak acids and the ratio of salts of weak acids to weak acids confirm Proctor's statement that babul bark contains catechol tans " (see Table 1). It gives a fission product of protocatechuic acid. With acid it hydrolyses into " reds," gallic acid and ellagic acid.

Some of the properties of babul bark are given in Table 1.

Burton and Barat[2] made a comparative study of babul bark, Mimosa and Myrob. Some of their results and also those of P. Sarkar [3] and those of P. Reddy, K. Joseph and K. Padmanabhan[4] are given in Table II. Burton and Barat observed that myrob liquor was much more buffered than babul and mimosa liquors and that the titration curve of babul bark liquor is similar but steeper than the mimosa liquor. Das and Barat[5] give 2.94 as buffer index for myrob and 0.52 and 1.01 for mimosa and babul bark respectively. They also give the titration spread (pH 2.0 to pH 5.8) for myrob as 505 compared to 203 for babul and 105 in the case of mimosa.

Use in the Tanning Industry

Regarding its use in the manufacture of leather, Edward, Bhadwar and Dey[6] record that babul had in the past very bad reputation. It is stated that it produced defects like bad colour and cracky leather which would tear. But now, it is agreed that with proper control, all these defects have been overcome and it is good for sole leather and light leather production, of course with a proper blend with myrob.

The author has made a study of sole leather tannage based on babul bark (using process followed in U.K. Tanneries) in National Leather Sellers College, London and has produced good leather with chemical analysis comparable with that of English Sole Leather *e.g.*, hide substance 30–32%. The author has also reproduced the results in KNIT Limited with success, of course, modifying the process to suit market needs. Thus it may be indicated that babul bark could be used for making good leather after suitably modifying it.

Previous attempts to manufacture extracts

Before discussing the pressing need and prospects of babul bark extract manufacture, it may be interesting to note that Edward, Bhadwar and Dey[6] and also F. Howes[7] record that a solid babul bark extract containing 46% tannin was prepared in India, but its preparation ceased during the trade depression of 1930's and no fresh effort has yet been made.

Need and prospects of babul bark extract manufacture

The modern advances in vegetable tanning have made it possible to produce any type of leather from any tanning material by suitably modifying its constituents. U.K. has produced "chestnut" extract from Mimosa by adding citric acid or formic acid to it. Similarly Italy has neutralised some acid of chestnut, to produce substitute for Mimosa. In Italy, an attempt is being made to evolve a commercial process to convert some of the acid in chestnut into salt using the well-known principle of Ion Exchange method. The author has used with success the English process of sole leather tannage, using babul bark after suitably modifying its acid and salt contents.

Apart from the need of modifying the properties of babul bark to suit the needs of tanner which could best be done by extract manufacture, there is the other side of the picture. And it is the colossal loss this nation is undergoing by throwing away tons of babul tannins into ovens on account of inefficient leaching in the tanneries.

The leaching efficiency in a leach house is 65–70% of the total solubles as given by the S.L.T.C. method. But the S.L.T.C. method again, in the case of babul bark, gives lower results compared with the efficiency of leaching which extract manufacturer would get. As an example, one sample of babul bark analysed by extract manufacturer for the purpose of extract manufacture gave 35% total solubles. The sample by S.L.T.C. method gave only 22.2%. The figures show that extract manufacture of babul bark is likely to be a paying proposition.

It is possible that we may be able to follow the example of Italy and make an attempt to develop an ion exchange method (commercial) to convert some of the salt in babul bark liquor into acid.

Myrob extract trade would gain indirectly from the babul bark extract manufacture. In the tannery leach house lots of myrob is being used along with babul bark, because the tanners have certain formula. Now, if babul extract is made and the extract manufacturers could fulfil the needs of the tanner, perhaps leach houses would be empty as they are in Europe and more of myrob would be processed extract in factories.

TABLE I.
Tannin Analysis of Babul Bark

S. No.	Analysed by	Moisture	Insolubles	Total solubles.	Tannins	Non-Tannins	Ash	Colour Y	Colour R	pH Analyt. Soln.	pH 20° BK Soln.	Acidity m1N/100 g. Tot. Sol. to pH 6.5	Acidity m1N/100 g. Tot. Sol. to pH 5.8	Salts m1N/100 g. Tot. Sols.	Remarks
1	Barat and Burton.	...	...	...	...	...	...	...	...	...	5.3	...	8.0	125	J.S.L.T.C., 1954.
2	Allegrini, Italy	8.8	56.30	34.9	22.3	12.6	...	...	...	4.70	...	42.90	...	85.9	For KNIT Ltd., Kapurthala (1955) (Filter Bell Method)
3	Self, at N.L.S. College, London.	9.6	62.70	27.7	14.1	13.6	...	...	...	5.06	...	18.50	10.0	84.5	1955
4	B. M. Das ...	7.8	71.20	21.0	12.41	8.6	6.62	28.7	16.2	...	...	...	...	...	Communication to Knit Ltd., Kapurthala. India, 1951
5	P. Sarkar ...	11.27	71.32	17.4	10.21	7.2	7.45	35.9	26.0	...	...	...	...	...	The Tanner June, 1952.
6	Reddi, Joseph and Padmanabhan.	10.00	61.46	28.54	20.60	7.94	...	15.5	5	4.00	...	...	...	...	The Tanner March 1956
7	Bayers, Germany.	14.00	57.10	28.35	18.25	10.00	...	...	...	4.85	...	...	...	...	Ref. Mr. Sahni.

(For more data on Tannin Analysis of Babul Bark—See *Indian Forest Records*, Vol. 1, No. 2, by Edwards, Badhwar & Dey.)

TABLE

Tanning Tests with

Raw material	Sampling position	Pre-Tannage		T A N		
		Liming	Deliming	°BK	Before pH	After
Indian Light Cow-hide	Official position	Straight for 12 days.	Saturated Boric Acid 18–24 hours and washed.	1% tan solution to 4% tan solution.	3.0	3.6
Ox butt ...	Butt range.	...	Full, with 3% Boric Acid and washed.	2.05% tan.	5.30	5.24
W/S Buffalo hides.	Full hide.	Straight for 14 days.	Surface with water only.	...	...	...

TABLE

Analysis of Leathers Produced in the

Moisture	Hide substance	Oils and fats	Water soluble	Insoluble Ash	Total Ash	Combined tannin
14.00	42.91	2.20	8.69	0.25	1.00	31.95
14.00	59.00	0.85	7.70	...	0.60	18.50
13.82	52.07	4.73	5.49	0.19	...	23.87

II

Babul Bark

NAGE						
Time of Comp. penetration	Speed of penetration	Yield on pelt weight	Goods suspended or laid flat	Ratio liquor to pelt	Finishing	Remarks
9 days ...	0.22 m.m. per day.	50.57% (14% moisture basis).	Suspended.	400 c.c. per 100 sq. c.m. pelt.	Surface dried with filter paper, oil and dry.	P. Sarkar. The Tanner, 1952.
Nearly four weeks.	...	36% after six weeks.	Suspended	6 : 1 ...	Surface dried with filter paper and dried in dark without oiling.	J.S.L.T.C., 1954 Burton & Barat.
...	...	42% after 3 weeks.	Laid Flat (E.I. Tanning method).	...	...	Reddy, Joseph, Padmanabhan.

III

above experiments

D.O.T.	Firmness	Tensile strength	Other properties	Remarks
74.45	Moderately soft non-cracky.	...	Quite suitable for commercial tanneries—already being used to the extent available.	P. Sarkar, The Tanner, 1952.
31.30	Fairly firm ...	Good after 5 days tannage, dropped considerably after 6 weeks tannage.	Produces well tanned, firm, dark brown leather, dark tea brown colour of babool leather would be regarded with disfavour in U.K.	J.S.L.T.C., 1954 Burton & Barat.
44.77	...	...	Possessed all the qualities of sole leather. Low D.O.T. and Reddish colour.	Reddy, Joseph and Padmanabhan.

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EVALUATION OF PROPERTIES OF NATURAL TANNINS BY MEANS OF FRACTIONAL TANNING

BY

A. N. MIKHAILOV

(*Moscow*)

ABSTRACT

Fractionation of natural tannins has been accomplished by fractional tanning, *i.e.*, by repeated immersions of different pieces of hides in the same tannin solution. The volume formation index and the shrinkage temperature of the leathers so obtained have been determined and compared with similar data for untanned hide. The results are used to evaluate tanning properties of tannins.

The development of production of tanning extracts in the Soviet Union is closely connected with the study of their tanning properties ; these are characterized by a number of quantitative indices. A series of the latter includes not only tannin content, degree of tannage and stability of the tannin-collagen compound to washing out with water, but also the capacity of transforming hide into leather. The latter property is characterized by a rise of the shrinkage temperature of collagen and by the volume formation in tanning, *i.e.*, the capacity of fixed tanning substances to preserve the porosity of wet leather, keeping it back from contraction during the removal of water by drying.

The rise of shrinkage temperature of leather as a result of tanning as well as its volume formation are the consequences of cross linking of protein molecules with particles of the tanning material fixed at a number of points. The shrinkage temperature of collagen is the most sensitive index of the intensity of intermolecular interaction in its structure.

The volume formation of leather as a result of interaction with tanning particles is explained by the decrease of compressibility of wet leather, which is a sequence of the formation of additional cross links in the structure of collagen and hence the rise of the resistance of the leather pores filled with water to contraction during drying caused by the forces of capillary pressure.

The quantitative evaluation of the volume formation in tanning can be made by determination of one of the following indices: the porosity of dry leather, its apparent density, its volume output (*i.e.*, the volume of leather expressed in cubic centimetres, that contains 100 g. of hide substance), the index of the volume formation in tanning (*i.e.*, the volume of a dry piece of leather expressed in per cent of the volume of the same piece in wet delimed condition.) The influence of various kinds of treatments on the volume formation of leather is still more pronounced in case of samples with greater natural porosity, (*e.g.*, goat and sheep skins, flanks of cow sides, etc.)

It is possible to determine the index of the volume formation in tanning and the shrinkage temperature of leather using the same samples. Typical values of shrinkage temperature and volume formation of leather treated by various tanning materials are given in Table I.

TABLE I

Characteristic of samples	Shrinkage temperature °C	Volume weight	Volume output	Porosity (Per cent)	Coefficient of volume formation
Vegetable tanned leather.	66–90°	0.65–0.85	250–400	50–60	0.95–1.10
Formaldehyde tanned leather.	75–90°	0.85–0.95	130–150	20–30	0.40–0.50
Leather tanned by auxiliary syntans and sulfite cellulose liquor, pH 4.	60–68°	0.90–1.20	120–200	25–35	0.40–0.60
Leather tanned by high quality syntans, pH 4.	70–85°	0.70–0.85	200–400	45–55	0.90–1.15

The importance of the quantitative indices of the tanning properties mentioned above can be illustrated by the results of the investigation of fractional tanning described below.

This investigation was carried out by the author of the communication together with Bachelor of technical sciences S. M. Bresler.

It is generally known that all natural tanning extracts used in tanneries always contain a number of different chemical substances that are fixed by the hide.

The inhomogeneity of natural tannins can be demonstrated even after their purification and removal of all non-tannins.

A chromatographic analysis shows very clearly the inhomogeneity of tannins. Dozens of spots showing an extremely complex structure of natural tannins can be seen on paper chromatograms. Till now the greater part of the components of the mixture isolated by chromatography of vegetable tannins are not identified.

If a piece of hide is immersed in an aqueous solution of natural tannins the protein will bind first of all the particles that have the greatest reactivity in the tanning process. The sorption of the less reactive tannin molecules by the protein will begin only after the removal of more active tanning components of the system.

In tanneries such kind of fractioning of tanning liquors takes place when untanned hide is treated in a direct current system. When tannage is carried out in the drum or in the counter current system, tannins are fractionated, although this process is more complicated.

Making use of this principle it is possible to accomplish fractionation of natural tannins by means of repeated immersions of little quantities of hide in the tannin solution removing in this way tannin particles of different, gradually diminishing reactivity.

The experiments described above were carried out to verify the existence of a correlation between the sorption activity of individual tannin fractions in the process of tanning and their tanning properties characterised by a rise of the shrinkage temperature of collagen and the index of volume formation in tanning.

Solutions of natural tannins, each containing 10–16 g. of tannin, determined by the shake method, were submitted to fractionation. For this purpose pieces of delimed goat skin of known volume, each containing 0.5–2.4 g. of dry protein were immersed for three days in a tannin solution. This time was sufficient to complete the tanning of the samples. At the end of this period the tanned pieces were removed from the solution, dried and submitted to determination of the volume formation index and the shrinkage temperature. After the removal of the first set of tanned pieces a new lot of delimed goat skin was immersed in the same liquor and the procedure was repeated. Every investigated tannin solution was utilised for tanning of 4–7 series of delimed goat skin pieces one after another.

The results of this experiment demonstrate that in all the investigated systems of tannins the capacity of tannin molecules to transform hide into leather closely correlates with their sorption activity in tannage.

The tannin fractions that are fixed by the first portions of the delimed skin show also the most pronounced capacity of tanning substances to transform hide into leather. The differences of the tanning action of the fractions compared are more pronounced in diluted tannin solutions.

The results of a number of series of experiments on fractional tanning are given below. (Tables 2 and 3).

Fractional tanning with solutions of Chinese tannins

Volume of solution 0.5 l, the contents of tanning substance 6 g per l. Each portion of delimed hide contained 1.2—1.5 g of dry protein.

TABLE 2

No. of fraction	Sorption of tannins (g. per 1 g. of dry protein)	Volume formation of dry leather (Per cent)	Shrinkage temperature of leather °C	Degree of detanning of the solution, (Per cent)	pH. of the solution after tannage
1	1.16	89.3	81	0.0	3.68
2	0.84	70.0	79	14.0	3.64
3	0.40	34.5	67	33.6	3.70
4	0.35	22.0	63	39.7	3.98

Fractional tanning with solution of oak wood extract

(Volume of solution 55 c.c., tannin content 4.64 g, pH 3.8. Each portion of delimed hide contained about 0.85 g of dry protein).

TABLE 3

No. of fraction	Sorption of tannins (g. per 1 g. of dry protein)	Volume formation of dry leather (Per cent)	Shrinkage temperature of leather, °C	Degree of detanning of the solution (Per cent)	Moisture content of leather per 100 g. of dry leather
1	1.32	112	77.0	0	142
2	1.17	102	76.0	28	143
3	1.07	99	75.5	46	158
4	0.85	...	76.0	66	174
5	0.62	78	73.5	83	183
6	0.41	65	70.0	94	194

The influence of fractional tanning on the shrinkage temperature and volume formation of hide samples treated in solutions of quebracho and oak wood extracts are shown in Figs. 1 and 2. The volume of solution in these experiments was 0.5 l with about 5 g of tanning substance. There was about 1 g of absolutely dry protein in each portion of delimed hide.

The differences in the properties of fractions are more strongly revealed when tannage is carried out in a diluted solution. It can be seen by comparing the results of fractional tanning of samples with oak wood extract, the tannin concentration being 84.4 g/l (Table 3) and 10 g/l (Figs. 1 and 2).

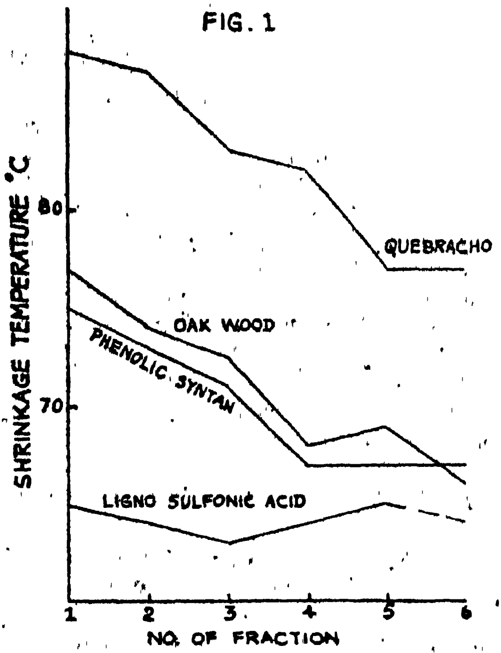
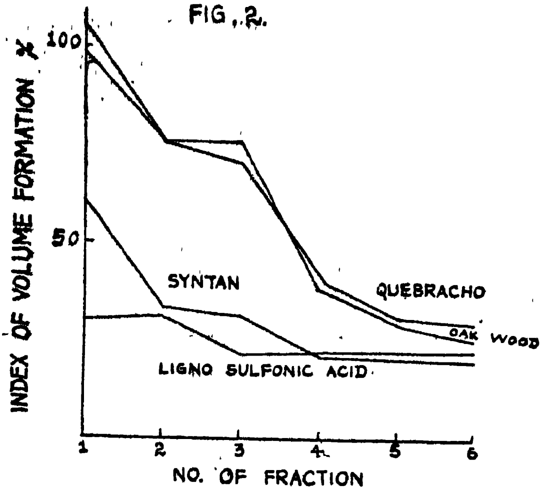


FIG. 1

The experimental data show that the tanning properties of different non-fractionated extracts are similar to the fraction that possesses the greatest sorption activity. The quantity of this most active fraction in a tanning extract is sometimes small. (20–30% of all the tannins present). These

FIG. 2.



findings show the possibility of considerably improving the tanning capacity of certain extracts of poor quality by adding small quantities of tannins which exert a good tanning action.

The results of the investigation mentioned above show usefulness of the method of fractional tanning for the evaluation of various natural tanning extracts and their mixtures.

DISCUSSION

Dr. D. Ramaswamy (C.L.R.I.) : (i) Is the fractionation technique employed similar to Page's method of determination of gelatin numbers? (ii) Is the difference in Ts with the different fractions due to the particle size being different or to specific chemical variations in the fractions ? (iii) Do the insolubles increase after each fractionation ?

Prof. A. N. Mikhailov : (i) The technique is similar to Page's method but with the latter, leathers could not be examined for their physical and chemical properties. (ii) The effect is due to change of chemical constituents and not to changing size of particles. (iii) The residual solution answers the usual tests for tannin ; but does not contribute towards tanning action that is increasing Ts or volume forming index.

Dr. Y. Nayudamma : I want to congratulate Prof. Mikhailov for his interesting and thought-provoking paper. Is dilution a factor in getting these results ?

Prof. Mikhailov : Even in more concentrated solutions the same tendency exists.

Dr. Y. Nayudamma.: Has any relationship been observed between volume formation and Ts for the groups of tanning materials ?

Prof. Mikhailov : There is no direct relationship, for example, in formaldehyde tanning, volume formation is higher if Ts is higher.

Dr. Y. Nayudamma : Has volume shrinkage been measured ?

Prof. Mikhailov : No.

Dr. Y. Nayudamma: If the Ts, the volume formation figure and the volume shrinkage of leather are obtained and correlated, it would throw more light.

Dr. S. Ghosh (C.L.R.I.) : Does the volume figure relate to the swelling of the pelt in the tan bath ?

Prof. Mikhailov : Sometimes it is true. But not generally. In formaldehyde tanned leather, the volume may be high after tanning ; but on drying, it will shrink to a very low volume. With vegetable tanned leather, the volume index is closely related to the volume in the tan bath.

Dr. S. Ghosh : What is the volume figure in the untanned pelt ?

Prof. Mikhailov : From 20 to 25 ; but the exact value depends upon the location of the sample and whether it is the buffalo hide or cow hide.

Dr. S. Ghosh : Is the penetration of the pelt by the tannin complete in the time interval allowed in these experiments ?

Prof. Mikhailov : Yes, for 3 days are allowed. With progress of fractionation, acid concentration becomes low and the rate of penetration slows down a bit.

Mr. R. Selvarangan (C.L.R.I.) : The paper is significant for the extract manufacturers, for myrobalan extract contains more of filling materials than tanning ones and it could be blended with some other tanning material so that both filling and tanning effects could be achieved.

Since the concentration varies from fraction to fraction, would the results be comparable ?

Prof. Mikhailov : There is the influence of concentration. However, the influence is pronounced with dilute solutions ; but not in these experiments.

Mr. R. Selvarangan : In sole leather tannage, the fourth fraction has got weight giving property, but very little tanning power.

Prof. Mikhailov : Volume formation in chrome tanning is accomplished mechanically. Some surface active agents are added.

Dr. S. K. Barat : The point raised by Mr. Selvarangan is a pertinent one. In the Page's method, there should be no variation in concentration. Was the relationship between concentration of tanned leather and the amount of tannin fixed, established ?

Prof. Mikhailov : A study of concentration tannin fixed is of great value. From Page's data we come to the conclusion that if we use greater concentration Ts varies a little. Our findings are that concentration is not an essential factor though it has some value.

Dr. S. K. Barat : In calculating fixed tannin, the first fraction is taken. Ts effects degree of tannage. Rise in Ts and rise in degree of tannage are simultaneous only upto a point. After that irrespective of fixation, Ts will show a constant figure.

Prof. Mikhailov : Dr. Gustavson has shown how the Ts rises in relation to the tannin fixed.

Dr. S. K. Barat : If tan liquor is analysed into different fractions and then pelt is taken and tanned in different stages we can know which has got the lowest affinity for pelt, which has got the highest affinity and which is responsible for the higher Ts.

Prof. Mikhailov : Your experiments are very interesting. If you take hide powder, by washing it with water, the volume forming property goes down.

PRODUCTION OF VEGETABLE TANNING EXTRACTS

BY

C. VALENTA,

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ABSTRACT

In order to achieve self-sufficiency with respect to tanning materials India has to produce extracts from tanning materials other than myrobalan, also either singly or in blends. Suggestions are put forth regarding regional survey of materials, trials with these on pilot plant and large scale, location of the extract factories and popularising the use of extracts.

In India at present only Myrobalan and Mimosa extracts are the two commonly used extracts. Of these only the former is being made in India and the latter is imported.

Although it is an accepted fact that free trade between countries on the basis of mutual help and friendship is the golden rule for economic success and one should never underestimate this statement, yet, it is quite natural that we should try to be self-sufficient and endeavour to reduce our imports. This objective cannot be achieved if we have only Myrobalan extract, because for the production of good sole leather a good blend of extracts is needed, as it is the experience of one and all of us that no good leather can be made with Myrobalan extract alone.

I feel that we will have to produce extracts out of other tanning materials that are available in India, with which the required blends for different types of tannage could be made, *viz.*, materials like Avaram, Babul, Mangrove, Divi-Divi and many other less known materials. According to information available there are more that 50 varieties of tannin bearing plants of economic importance to India. A systematic survey of all these on a state and regional basis is of paramount importance to the tanning industry of this country.

The manufacture of tanning extracts should not at all discourage or impede the progress of the village tanner or the cottage industry. On the contrary it is to assist him in getting used to better and more practical ways of tanning. The Small Scale Industries Service Institute (Leather Department) could be entrusted with the task of popularising these extracts with the Cottage Tanning Industry.

The extracts may be made from one or many tanning materials at a time (*i.e.*, Blended extracts) as suggested by the Assistant Director-in-Charge of the C.L.R.I. at the Symposium on Industrial Leathers at Calcutta.

I would like to point out that it should be possible to establish the Extract Factories at the spot where the tannin bearing plants are available, which will save unnecessary transportation charges and at the same time will give employment opportunities to people in these usually undeveloped or underdeveloped areas.

The Research work according to my opinion is difficult to carry out at one place in such a large country like ours. So it is my suggestion that under the direction and supervision of some Central-body, say the Central Leather Research Institute, regional sub-committees should be formed to survey their respective localities, do the preliminary analysis and send sufficient quantities of tanning materials giving all the available details like botanical name, age of the plant, quantities available per year at present and plantation possibilities, etc., chemical and any other technical data worked out, to the Central-body, where the problem of utilisation and how best, could be tackled, in the way of pure extract manufacture and also blends, as also pilot scale tanning experiments.

Later, the organised sector of the tanning industry can be requested to try the same in their factories for large scale trials. If found satisfactory, the manufacture of such economical extracts can be put on a commercial scale and thus serve the leather industry.

It is hoped that the organised sector of the Leather Industry will give all support and help for this purpose. I can assure you that our organisation Bata Shoe Company Private Limited, will be pleased to give all assistance and co-operation needed as for instance by way of conducting Pilot scale and if necessary large-scale trials in its factory.

It may be interesting to know that some few years ago Italy was facing similar problem how to replace Quebracho. Germany and the countries occupied by them had to replace over 25% of Tanning extracts used, by Syntans and Barks, and Brazil, being in short supply of Quebracho was in similar position as we are at present, and solved it successfully. Active steps have been taken first to survey the Tanning material resources and possibilities of extract manufacture in the country and then the plantation of some new species were started to satisfy the demands and requirements of the Tanners.

Similar steps may be taken also in India for a speedy and efficient building up of a sound leather production.

THE NEED TO CHANGE OVER TO VEGETABLE TANNIN EXTRACTS

BY

E. C. MATHEW & M. K. UDAYA VARMA

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ABSTRACT

At present Indian vegetable tanning industry is confronted with a serious shortage of tanning materials. To partly surmount this, a plea to the Indian vegetable tanning industry to change over to the use of extracts is made.

Of late the Indian vegetable tanning industry has been experiencing an acute shortage of tanning materials. The reasons as well as the remedies for this are many. This shortage could be surmounted partly by the utilisation of the many substitutes for wattle bark, and partly by the use of extracts or leach liquors. The East India tanning industry consumes the bulk of the tanning materials. As the contact system is adopted in E.I. tanning, a good portion of the tannin is lost in the spent tanning material because the material is not completely leached. The analyses of a few fresh and spent barks are given below :

	Percentage of tannin in		
		Spent Bark	
	Fresh bark	First bark	Second bark
Avaram	16.8	7.0	9.3
Konnam	11.0	5.0	6.0
Wattle	32.0	11.0	19.7
Karada	28.0	7.0	10.0

Thus it may be seen that about 50% or even more of the tannin is wasted in the second bark. This wastage may be still more at the myrobing stage. Hence, it is high time that the E.I. Tanners changed over to the use of extracts or leach liquors in place of the tanning materials to get over the shortage.

Two days ago an E.I. kip tanner has pointed out in the local dailies that the cost of production of kips is going up. The use of extracts or liquors is bound to bring down the cost of production also.

However, the problem is not very simple. The industry may not readily accept this suggestion for fear of detrimental effects, on the mellowness and other unique properties for which the E.I. tanned leathers are renowned. By suitable adjustments it is possible to produce good quality E.I. tanned leather by using extracts or liquors for the tannage.

India is a country of distances and as such, large quantities of vegetable tanning materials are being transported along the length and breadth of the country. This involves a lot of unnecessary freight charges which could be avoided by the change over to the use of extracts.

As already pointed out by Mr. Selvarangan, the manufacture of blended extracts is to be considered. Blended extracts are very popular in the United Kingdom where Messrs. William Walker and Sons Ltd., are marketing a variety of blended extracts meant for different purposes.

NEW TANNING MATERIALS

BY

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ABSTRACT

The data on the use of three new tanning materials, *viz.*, Xylia Xylocarpa, Terminalia paniculata and Terminalia tomentosa are presented.

The vegetable tanning industry in India is one of the major industries of the country. It earns a considerable amount of foreign exchange. Madras alone is exporting annually vegetable tanned leather worth Rs. 25 crores. This industry was built up on Avaram (*Cassia auriculata*) and Konnam (*Cassia fistula*) barks in the south and Babul (*Acacia arabica*) bark in the north. Since the available avaram and konnam barks were not sufficient to tan the immense quantities of Madras tanned kips required for the military during World War I wattle bark was imported from South Africa and was successfully used for tanning kips. Later the tanneries in North India—Cawnpore etc., which were depending entirely upon babul, took to wattle tannage and a stage came when almost every bark tanner found it impossible to do without wattle and thus, wattle came to stay. Realising this drain on the national exchequer, the Madras Government started extensive wattle plantations in the Nilgiris, Palni and Kodaikanal hills and also took measures to encourage more and more cultivation of wattle. Consequent on the cessation of trade relations between India and South Africa, the Industry had to face a crisis and now Kenya is the Indian Supplier of wattle bark and its extract. The quantities of wattle bark and its extract imported during the years 1953–56 with their values are given below :

Import of Wattle

	1953–54		1954–55		1955–56	
	Quantity	Value	Quantity	Value	Quantity	Value
	CWT.	RS.	CWT.	RS.	CWT.	RS.
Bark ...	76,119	20,23,826	76,687	19,55,163	54,390	37,80,771
Extract ...	293,412	91,07,361	107,970	59,34,763	249,209	78,55,262
Total value ...		11,131,177		78,89,926		11,536,033

Thus it may be seen that in spite of the extensive wattle plantation referred to above, the industry still vitally depends on the import of this very valuable material.

With a view to making the country self-sufficient in its requirements of vegetable tanning materials, a vigorous search of raw tanstuffs was launched at this institute since its inception and a number of valuable new materials have already been reported. Persistent work in this direction has shown that the following three tanstuffs which are available in plenty in the forests of Kerala State can solve the problem further. The samples used for the experiments were got from the Kottayam District of Kerala State.

I. Terminalia paniculata

Vernacular names are Pumarudu, Venmarudu (Tamil and Malayalam), Pulamaddi, Nimiri (Telugu). The analysis of the sample is given below :

Moisture : 10 per cent.
Tannin : 14 per cent.
Non-tans : 5.4 per cent.
pH of analytical solution : 4.6
Colour of analytical solution : Y-28 ; R-9
Free acids (to pH 5.8): 24.5 mgm. eq./100 gms. total solubles.
Total salts (sulphated ash method) : 129.2 do.
Salts of weak acids (to pH 2.0) : 83.3 do.

Tanning experiments : A wet salted cow hide was soaked in plain water, washed well and limed according to the traditional two pit straight lime system adopted for E.I. tannage. They were unhaired on the 8th day and fleshed after another six days. 4″ × 3″ pieces were cut from the butt portion, delimed with boric acid and taken for tanning using Terminalia paniculata bark.

Bark equivalent to 16% tannin on the fleshed weight was used for the first bark. This was soaked in water on the day previous to the commencement of tanning. The liquor was adjusted to 7° BK and the tanning started. For the second bark, material equivalent to 8% tannin was soaked in old liquor.

The barkometer was 10°. On the 14th day the leather was taken out, bleached in a solution containing 2% Perfectan 0 and 1% oxalic acid, beamed and put in myrobalan liquor of 20°BK. On the 16th day it was beamed, oiled with pungam oil and dried.

The leather produced was of a very light colour. So this bark was used in the E.I. tannage of sheep skins. Tanning, etc., were done exactly as described above.

The leather was analysed and the results are given below :

Moisture : 12.95 per cent.
Fats and oils : 8.37 per cent.
Water solubles : 12.8 per cent.
Insoluble ash : Nil.
Hide substance : 37.44%
Fixed tans : 28.44
Degree of tannage : 75.95
pH of water solubles : 3.85

Experiments were also carried out to further improve the tannage by blending as follows :

I Terminalia paniculata plus Avaram 1 : 1
II Terminalia paniculata plus Konnam 1 : 1
III First bark avaram and second bark Terminalia paniculata.

From the point of colour, III was as good as pure avaram tannage (control); II was superior to control as far as fulness and feel were concerned but the colour was not as good as that of the control.

Thus Terminalia paniculata alone could be used for the E.I. tannage of kips and in blends with Avaram or Konnam for the E.I. tannage of skins.

II. Terminalia tomentosa

The vernacular names are Karimarudu (Tamil and Malayalam), Asana (Sanskrit) and Nallamaddi (Telugu).

Bark from young and old trees gave the following analyses :

	Tender bark	Mature bark
Moisture	10%	10%
Tannins	17.97%	25.64%
Non-tans	5.41%	4.51%
pH of analytical solution	4.7	4.6
Colour	Y-39 R-20	Y-13 R-8

Tanning trials with this bark were done using

1. Terminalia tomentosa alone
2. „ plus Myrob 3 : 1 (parts by weight)
3. „ plus Myrob 2 : 1 „
4. „ plus Dhawa 1 : 1 „

Tanning, myrobing, etc., were done as detailed earlier.

Tanned with Terminalia tomentosa alone, a light coloured leather is produced which is slightly pinkish. By blending, the colour is improved but the penetration is poor in all the cases. As the leather is very firm, this material may be more suitable for sole leather tannage. Because of the high T/NT value, manufacture of extract from this bark should be feasible.

III. Xylia xylocarpa

Vernacular name Erumullu (Malayalam) ; analysis shows that it contains:

Moisture : 10 per cent.
Tannins : 17.1 per cent.
Non-tans : 11.1 per cent.
pH of analytical solution : 5.2
Colour of analytical solution : Y-25 ; R-12

E.I. tanning experiments with this bark in blends with Konnam bark and Dhawa leaves and myrobalans are very promising. The leather produced is very fine grained and light coloured. Detailed work on these materials is in progress.

ROT—RESISTANT INSOLE LEATHERS—SOME RECENT DEVELOPMENTS IN SOUTH AFRICA

BY

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Perspiration and iron grindery are amongst the causes of deterioration of conventional insole leathers : seepage water of low pH value also comes into the picture in the case of mineboot insoles. Two tannages, novel in the field were tried—a zirconium tannage and a chrome pretannage followed by retanning with a non-iron reactive replacement type syntan. While initial trials showed both these to be promising, exhaustive laboratory field tests decided in favour of the chrome-syntan combination tannages. The two commendable features of products of the latter type of tanning are high and rapid absorbancy of the insole leading to quick removal of perspiration and absence of cracking. Though the cost of insole leather so prepared is a little greater than that of the conventional type, this increase in cost is offset by the great improvement in serviceability. Even in regard to properties like wet stitch tear strength, tensile strength and elongation at break, the insole leathers prepared by the new method retain almost completely their original characteristic, after use for 3 months.

The basis of the process is the retannage of chrome leather, prepared with 2% Cr_2O_3 on limed weight, with 10–15% of a replacement syntan which is not reactive to iron. The pH of the syntan should when necessary be adjusted to about 3.5 before retannage. The leather so produced can be coloured and a light fatliquor of about 2% is usually sufficient. Finishing is normally confined to buffing on both sides and the fine nap which is produced is very attractive.

In general, this should be considered as an adjunct to the chrome side leather tannery. Particularly where low quality hides are being used, leather unsuitable for upper leather can be sorted out in the blue and finished as chrome-syntan insole leather. This type of leather can be dried by a pasting process and for most civilian work, some sulphite cellulose can be incorporated to replace part of the syntan to reduce the cost, at the expense of firmness.

IMPREGNATION OF SOLE LEATHER

BY

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ABSTRACT

The advantages of treatment of leather with synthetic and natural resinous materials are discussed. The various methods by which the resins could be incorporated into the leathers are described with specific samples developed at the Institute.

Most of us are aware of the great change-over from the old to the modern type of sole leather. For a long time the yield and the colour of the leather have been the only questions which interested tanners of sole leather. The traditional methods of sole leather tannages, involving tanning for a period of 30 to 34 weeks are being replaced by modern rapid tanning methods reducing the time of tannage to five or six days, though there is much controversy in regard to the quality of rapid tanned sole leather. These criticisms appear to be that these leathers are softer, wearing quality poorer and water absorption and loose tans being higher in the rapidly tanned leathers as compared to the traditional slow tanned leather. The argument as to whether sole leathers tanned by the old method or modern methods differ in their wearing properties has never been finally settled one way or the other. Our own experience has been that the so-called Bag tanned sole leather which is cheap and flexible, has wearing properties equal to if not better than the traditionally tanned sole leather, though of course the water absorption of the same has been very high as compared to the fine variety of sole leather, a serious drawback indeed. There is unfortunately very little information available regarding the connection between hide origin, the kind of tannage and the technique of tannage on the one hand and serviceability on the other. The conquest of part of sole leather market by rubber and plastic industries, now brings the sole leather industry face to face with the serious problem of producing a product which is as flexible, waterproof, wear resistant as a synthetic sole. In U.S.A., U.K, and European countries there is a distinct tendency towards the use of flexible soles. Apart from the advantage to the footwear manufacturer, a flexible sole definitely gives more comfort as compared to the former variety. But the disadvantage of a flexible sole would be its higher water absorption as compared to the synthetic soles. It is well recognised that treatment with polymers increases the abrasion resistance and decreases the water absorption of sole leathers thus improving greatly their quality. It is felt that if the demand for flexible soles is to be met successfully, it can be done by the treatment of leather with synthetic resins either before or after tanning. It is expected that treatment with certain types of resins will be able to keep the leathers flexible, increase their abrasive resistance, decrease their water absorption whilst maintaining more or less unchanged the porosity of the leather. This last property is the main advantage of leather when compared with plastics. Thus we are not far away from the idea of uniting leather with modern plastics. In the U.S.A., much work has been done on the impregnation of leathers with resins to give these valuable additional properties to leather and pilot plant scale production of such leather is being carried out. In the United Kingdom, Germany and other places researches are being carried out, unremittingly to impregnate leathers with resins and make them flexible, durable and waterproof to meet the competition from the synthetic soles.

Resin products are also being developed to fill the inferior and loose upper leathers and convert them to fuller and superior quality upper leathers.

In India this problem of filling is all the more important since the majority of the hides are fallen and consequently poorer in substance and hence need filling to improve the quality. In the U.S.A. and United Kingdom and Europe, they have the advantage of highly developed chemical industry, which carries out researches and develops new products for the use of the leather industry. In U.K., the I.C.I. which is a huge chemical concern, carries out researches and develops products for the leather industry. They are also working on this problem of impregnation and filling and have already developed a product 'Bedafil' useful for impregnation of sole leathers. Similarly several firms in Germany, are working on this problem. Synthetic waxes useful for purposes of impregnation have been developed. The process also is comparatively simple and quicker. The wax is melted and the leathers are dipped for 2 to 3 minutes in the molten material. The leathers treated in this way have improved abrasion and water resistant properties and at the same time are quite flexible. This appears to be a very useful method of impregnation as it involves the use of no solvents and is very much quicker. With the availability of paraffin wax and shellac waxes in our country, it should be possible to develop suitable impregnants from the same by modification of their properties. Though at the present moment, we do not have the necessary raw materials for the manufacture of synthetic resins, with the expansion of petroleum refining in India and attendant availability of raw materials for the manufacture of polymers, there is a great future for impregnated leather both in meeting competition from non-leather soling materials and in the upgrading of the quality of poorer leathers. Further, fortunately, we have plenty of natural polymeric substances like Shellac, Rosin and rubber latex, which by suitable modification of their properties could be used as impregnants.

In our country, we have a variety of sole leather called the Bag tanned sole leather which can be economically manufactured. It is flexible, with wearing properties equal to those of the traditionally tanned sole leathers, the only disadvantage of the same being its very high water absorption property which makes it unsuitable for wet weather. If this type of leather could be impregnated with suitable impregnants and improve its waterproofing properties, it would compete successfully with the non-leather soling materials that are taking the place of leather. In our country as the living standards increase and more and more people take to footwear the demand for good quality soles is bound to increase and perhaps the only way with which this can be met may be by impregnating the leathers with resins, synthetic and natural.

. In view of the importance of this problem to the Indian leather industry a literature survey of the problem has been carried out and a few experiments carried out with a few synthetic and natural polymers.

There are mainly two ways in which impregnation with polymers can be carried out. Either the leather is treated with a monomer which is subsequently polymerised within the leather or the polymer itself used for impregnation. Naturally much variation in the degree of the polymerisation of the material used in the latter case can occur and in fact a process can be visualised in which a polymer of a low degree of polymerisation is applied and subsequently polymerised further *in situ*. Preformed polymers can be employed either in solution in an organic solvent or in the form of an emulsion in water. The latter is preferable for several reasons, namely the greater accessibility of the structure of the leather in aqueous media, the avoidance of fire risks and the lower cost. Both methods were tested. Polyisobutylene, Polystyrene, and Polyvinyl acetate, were dissolved in suitable solvents and leathers we retreated with the same. In each case the water absorption was lowered by about 50%

and the abrasion resistance also improved. The desired flexibility was however not obtained. A resin prepared from natural shellac and Bhilawana and cashew shell oils, both indigenous materials, has been found to be a good impregnating agent for sole leathers as good as Vistanex used by the N.B.S. America Leathers treated with solution of the same in Toluene have been found to improve the water absorption and abrasive resistance properties. The colour of the leathers was however a bit dark but this could be remedied by a surface bleach using a bleaching system. The leathers in this case retained their flexibility. Impregnation was also attempted with solutions of Rosin in toluene and the treated leathers though improved in water absorption and wearing quality were however a bit stiff and not flexible. The technique of impregnation of the above type was very simple. Solutions of polymers were made in toluene (about 30% resin solutions have been found to give reasonable uptake of 15% to 20% and the desired flexibility and improvement in water absorption and abrasion resistance) and the samples of vegetable tanned crust sole leathers were then kept in the solution for 14 to 18 hours at room temperatures. The pieces were taken out, excess polymer wiped off and the samples dried in air and weighed. From the increase in weight the uptake of the polymer by the leather was obtained.

Though it is true that far-reaching improvements could be obtained by impregnation in organic solvents, it would appear that work in aqueous phase will have to be the chief aim. It should be possible to produce aqueous emulsions of suitable particle sizes from resins like shellac and rosin which will be useful for incorporation in the leather and thus improve the quality of the leather.

As an example of application of emulsion of polymers for impregnation of sole leather, natural rubber latex was chosen and experiments were carried with the same for impregnating the leathers. But natural rubber latex has certain disadvantages for purposes of impregnation. It is stable in alkali and as such unsuitable for impregnation in vegetable tanned sole leathers as in the alkaline medium, tannins are stripped and the treated leathers become dark in colour. This was overcome by the use of stabilisers, which when added to latex keeps the latex stable even in acid conditions. The other disadvantage was the lack of penetration into the leather as the molecular size of the latex particles was too big. The treated leathers were found to have only a surface deposition and this was overcome however by the use of skimmed latex which has a smaller particle size and with the leathers treated with skimmed latex, there was an uptake of 5 to 6%. The treated leathers were found to be having improved waterproofing properties and at the same time flexible.

The technique of polymerisation *in situ* starting with a monomer was also tried. The sample of leather was immersed in the purified monomer containing a catalyst usually Benzoyl peroxide. The sample was removed after ½ hour, excess polymer wiped off and placed in a vessel in which air was displaced by H_2 and the vessel was kept at a temperature of 45 to 50°C overnight, cooled and weighed. The difference in weight gave the measure of the polymer deposited inside the leather. Butyl Methacrylate, isobutylmethacrylate, Vinyl Acetate have all been tried and Vinyl Acetate was found to be very promising.

But as earlier pointed out, work in aqueous phase will have to be the chief aim in order to create radically improved sole leather. The impregnating processes will play an important part in this connection in future, but all the contributory factors which appear to be of use in improving serviceability should be compiled and utilised.

RAPID SOLE LEATHER TANNAGE USING WATTLE SUBSTITUTES

BY

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ABSTRACT

Rapid tannage of sole leather has been done using Pithecolobium dulce, Peltophorum ferrugineum and Karada barks. The data is presented.

Two of the wattle substitutes, *viz.*, the barks of *Pithecolobium dulce* and *Peltophorum ferrugineum* have been successfully used for sole leather tannage by the normal method. As rapid tannage of sole leather has come to stay, these two materials and another substitute *viz.*, Karada bark have been tried singly and in blends, among themselves and with Babul bark, for rapid tannage of sole leather. The right halves of hides were used for experiments with these barks and the left ones for the control *i.e.*, wattle tannage. In both the series of experiments, each side was cut into 9 pieces of about 16″ × 16″ and all the pieces were tanned to get the correct idea of the yield, which is very important in sole leather tanning.

Experimental

Wet salted buff hides were soaked in water for 6 hours, washed well, drained, weighed and cut into sides.

Liming

The sides were limed in once used 2nd lime liquor with addition of 6% slaked lime, and were handled twice. On the 2nd day 1% sodium sulphide was added and the sides were handled in the evening and on the following day also. They were unhaired on the 4th day and relimed in a fresh bath with addition of 12% slaked lime and 1% caustic soda and handled twice. They were handled on the 5th day also.

Fleshing and deliming

On the 6th day they were fleshed, weighed, washed and left overnight in water. Next day they were washed for a few minutes, scudded and left overnight in water. On the 8th day they were washed for a few minutes, scudded, and delimed with 1½ to 2% sodium bisulphite and 1 to 1½% boric acid. When ¼ of the total thickness was delimed, ½ to 1% of formic acid was added. When ⅔ of the total thickness was delimed, the sides were scudded, washed and cut into pieces.

Tanning

The pieces were suspended in 10° BK liquor and handled for one hour. They were handled several times on the next day. They were beamed and suspended in 20°BK liquor on the next day and handled. Handling was done on the following day also. They were laid flat in 30°Bk liquor on the next day and thereafter the strength was raised by 20°BK every alternate day. After having kept in 70°BK liquor for two days, the liquor was strengthened to 70°Bk and the pH adjusted to 3.5 by addition of formic acid and the sides were kept in this liquor for 2 more days.

Myrobing

First they were myrobed for two days in once used myrob liquor of 65°BK and then myrobed for another two days in fresh myrob liquor of 70°BK.

The pieces were washed well, piled for two days, oiled in the drum and hung up to dry. When sammed, they were set thrice and allowed to dry completely. When dried, they were seasoned and rolled.

Experiments were carried out using the following tannages :

(1) Pithecolobium dulce plus myrob ;
(2) Pithecolobium plus babul plus myrob ;
(3) Peltophorum ferrugineum plus myrob ;
(4) Peltophorum plus babul plus myrob ;
(5) Karada plus myrob.
(6) Karada plus Pithecolobium plus myrob ;
(7) Karada plus babul plus myrob .
(8) Karada plus Peltophorum plus myrob ;
(9) Pithecolobium plus Peltophorum plus myrob.

The following Table gives the yield.

	Pithecolobium dulce	*Control*
(1)	69%	67.5%
(2)	66%	64.0%
(3)	66.5%	66%
	Peltophorum ferrugineum	*Control*
(1)	71%	65.5%
(2)	66.5%	66.7%
(3)	70.4%	69.1%
	P.d. plus Babul	*Control*
(1)	69.5%	68.2%
(2)	67%	67.4%
(3)	68%	65.5%
	P.f. plus Babul	*Control*
(1)	72.5%	73%
(2)	67%	64.5%
(3)	68%	67%
	Karada	*Control*
(1)	66.2%	68.3%
(2)	66.5%	68.7%
(3)	66.6%	68%
	Karada plus P.d.	*Control*
(1)	66.1%	69.4%
(2)	69.5%	71.5%
(3)	64.1%	63.6%
	Babul plus Karada	*Control*
(1)	66.7%	66.7%
(2)	66%	66.5%
(3)	67%	66.7%

	Karada plus P. f.	*Control*
(1)	67.4%	66.7%
(2)	68.0%	67%
(3)	68.0%	66.5%
	P. d. plus P. f.	*Control*
(1)	66%	61.7%
(2)	65.3%	63%

It may be seen that the yield is higher in almost all the experiments except with Karada. The colour, general appearance and feel of the leathers are better in almost all the experiments. The chemical, microscopical and physical tests of all the leathers are in progress and it is hoped that the experimental leathers will be as good as, if not better than, the control.

SOME THEORETICAL CONSIDERATIONS PERTAINING TO THE MODIFICATION OF LIGNIN SULPHONATES FOR TANNING PURPOSES

BY

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ABSTRACT

Commercial waste sulphite liquors from the paper industry provide an abundant source of Lignin sulphonic acids and their salts, which may be suitably utilised as a raw material for potential tanning agents. Various possibilities of modifying this material chemically have been discussed in the light of hydrogen bonding theory of tanning mechanism.

Although quite a variety of indigenous tanstuffs are available, the Indian tanning industry is considerably dependent on the imports for its supply of quality vegetable tanning materials. This is mainly due to the fact that apart from their inherent deficiency in some form or other, most of our tanniferous trees come from wild stands and as such their supply is rather sporadic in nature. (The prospect of meeting the balance of our requirements at high cost by imports is bleak). With the possibility of a future shortage in the world supply of vegetable tannins looming large, the need for some phased programme to combat the situation is obvious. The problem can be viewed in its two perspectives. One way to approach this problem would be to develop suitable strains of indigenous substitutes by propagation and cross-breeding experiments and to raise these natural vegetable tannins in plantation so as to ensure a regular supply of these materials to the industry. Alternatively, the problem can be tackled by developing such synthetics which would successfully replace the vegetable tannins altogether or could be used advantageously in conjunction with cheaper and inferior materials to yield good quality leather. Research in both these directions is in progress at the Central Leather Research Institute and the results so far obtained are promising. Various types of synthetic tanning agents of the phenol-aldehyde type have been prepared which may meet the requirements of the commercial leather manufacture. However, the relatively high cost of raw materials and of manufacture may make the use of such syntans prohibitive, specially for heavy leather tannage.

From an economic viewpoint, therefore, one has to consider the possibility of utilising the low cost commercial bye-products, and in this respect, the lignin wastes, being the cheap and plentiful bye-product of the paper industry, are already in use as an extender for the natural tanning materials. The utilisation of these wastes, commonly known as sulphite cellulose extract or the waste sulphite lye will prevent any critical shortage of tanning materials as well as solve the effluent disposal problem faced by the paper industry. The lignin waste thus appears to be a promising raw material for the production of potential tanning agents both from a practical as well as economic point of view.

The structural similarity between the natural tannins and lignin was demonstrated as early as 1937 by Freudenberg who concluded that the tanning reaction by lignin sulphonic acid occurs mainly at the free amino groups of the hide protein owing to the presence of large number of sulphonic hydroxyl groups in the molecule. The inadequate number of phenolic hydroxyl groups in the lignin molecule stands in the way of obtaining superior leathering properties by this material, as postulated by the hydrogen bonding theory of tanning mechanism. The decreased tear resistance and the undesirable hydrophilic characteristics of the leather tanned with lignin sulphonic acid as it is, are attributed to its amino specificity and high content of secondary and tertiary alcoholic groups respectively. With sufficient evidence in favour of the theory that hydrogen bonding at the peptide link is in the main responsible for the tanning action, it is felt that proper chemical modifications of lignin sulphonic acid will lead to an improved product that will overcome the objections associated with the unmodified material. Naturally, it will be necessary to modify these materials in such a way that their capacity to hydrogen bond at the peptide link will be enhanced.

At the outset, it is important to mention that the commercial lignin wastes should possess a fairly constant composition so that reproducibility of any chemical process may be ascertained. This is feasible in our country, as the sulphite process of woodpulping has been thoroughly investigated and standardised so as to give a bye-product of standard composition as required. More commonly, these wastes consist of a magnesium salt of lignosulphonic acid.

Having established a satisfactory source of raw material, let us turn our attention to the specific chemical reactions that will convert lignin wastes to potential tanning agents. These reactions should be so designed that the product of the particular type of modification with increased ratio of phenolic hydroxyl groups assumes an optimum particle size and at the same time retains the water solubility of unmodified lignin sulphonic acid. A chemical modification that would reduce the amino specificity of lignosulphonates and subsequently enhance the hydrogen bonding ability consists in minimum desulphonation. This would involve only partial removal of sulphonic groups so that water solubility would not be too greatly reduced. In practice, the waste lye can be refluxed with KOH solution to the required extent and subsequently acidified with any acid.

Another method of decreasing amino specificity and creating additional hydrogen bonding loci would be the condensation of the sulphonic acid groups with phenolic substances to form sulphones. Investigations concerned with the sulphone bridge type of syntans support the view that this type of modification will increase the tanning potential of lignin materials. Simultaneously, the particle size of the lignin units will also be increased and this is presumed to be advisable. Attempts to utilise the spent tanliquors for this purpose may be of interest not only because they are rich in polyphenolic bodies but are also readily available as tannery wastes. While selecting the phenolic substance, it may, however, be remembered that maximum effectiveness of the modification can be had if the phenolic hydroxyl groups lie para or ortho to the methylene bridge.

The condensation of the phenolic-aldehyde type polymer with the lignin materials would also yield valuable results. In some of the preparations of replacement syntans, these polymers may be merely blended with lignin wastes. The formation of a phenolic-aldehyde component in the lignosulphonate itself may possibly eliminate the difficulty of retaining water solubility as afforded by the dispersing action of the lignosulphonates.

Lignosulphonates can also be converted to their chloro derivatives under certain conditions and a further treatment of such derivatives with caustic alkalies would hydrolyse them to the corresponding phenolic derivatives which might as well be desulphonated during the course of hydrolysis. The possible modification of the sulphonic acid group of the lignin sulphonates to the sulphonamide through the sulphonyl chloride also deserves mention, and might be of value in heavy leather tanning.

The modifications of the lignosulphonates discussed above are unique in that they concern the sulphonic acid portion of the molecule alone. Other types of chemical reactions are, of course, important and may involve the removal of methoxyl groups, formation of an ester with the alcoholic hydroxyl groups of lignin, nitration and so on. Demethylation of lignin sulphonic acid to increase its phenolic hydroxyl content might be difficult to justify owing to the high cost of the suitable demethylating agents and in view of the drastic nature of reaction involved. In addition to the drastic effects on the lignin molecule any traces of the reagents used for demethylation in the final product may tell upon the quality of the leather produced with it. When treated under mild conditions of alkaline and acid hydrolysis, the degree of hydroxylation of the lignin material was found to be very low as supported by little improvement in the leathering properties of the raw material. The chemical reactivity of the several alcoholic groups of the lignin molecule permits combination with carboxylic and sulphonic acid chlorides to form esters. By proper selection of the reagent, *e.g.*, the 2, 4 dihydroxybenzoic acid and its chloride, the phenolic hydroxylation of the lignin sulphonic acid may readily be achieved. The lignins can readily be nitrated too and considerable degree of hydroxylation may be effected through diazotisation of the reduced nitro derivatives.

In the light of the varied nature of chemical reactions and processes discussed above, and directed towards improvement in the tanning characteristics of lignin sulphonic acid and its salts, a detailed programme of study has been chalked out in our laboratory with the hope that the tanning industry of the country will be largely benefited.

ASSESSMENT OF THE TANNING POTENTIALITY OF SOME MODIFIED LIGNOSULPHONATES

BY

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ABSTRACT

The hydrogen bonding theory of phenolic tannages has led to believe that the absence of real tanning properties in Lignin sulphonic acid is due to the inadequate number of phenolic hydroxyl groups in the Lignin molecule. Various derivatives of Magnesium lignosulphonate with high phenolic content were prepared, following condensation with phenolic substances such as Resorcinol, Phenol, polymeric phenol sulphonic acid and so on. The preliminary evaluation of tannery potential of these modified Lignosulphonates was done on the basis of their ability to combine with gelatin. Actual tanning tests with these materials were also performed using delimed goat skin pieces, and their tanning characteristics have been discussed with reference to certain physical properties of leathers produced.

Sulphite cellulose extracts or the commercial waste sulphite lye, which are rich in lignosulphonates, come as an abundant waste of the paper industry. The tanning potential of these waste liquors has been widely studied and demonstrated. However, the absence of any real tanning properties in lignin sulphonic acids, the chief constituent of the sulphite lye, has been discussed by a number of investigators who invariably conclude that this is due to the relatively low ratio of phenolic hydroxyl groups. The tanning properties of lignin sulphonic acid are attributed to the presence of sulphonic and phenolic hydroxyl groups, although the latter are in much smaller a percentage as compared to the natural tannins.

Tu and Lollar[1] have pointed out that in the heterogeneous system existing during tannage (*i.e.*, protein, tannin, non-tannin and solvents) there are many active centres at which, it is possible to speculate, the reaction between tannin and collagen occurs. The free amino and carboxyl groups, the guanidyl groups, hydroxyl groups, and the peptide link itself are all possible reaction loci. Such heterogeneity does not indicate that vegetable tannage occurs by a single mechanism but the data of the above workers clearly indicate that, in the case of the phenolic tanning materials studied, hydrogen bonding of the phenolic group of the tannin to the protein, possibly at the peptide backbone of the collagen, plays a very significant role. This hydrogen bonding theory of tannage tends to the belief that a chemical modification of lignin sulphonic acid to yield products similar to the higher polyphenols, and the polymeric aromatic sulphonic acids (*e.g.*, the natural tannins and the syntans) would result in an effective tanning agent. Such a view has been further supported by recent research concerned with the tanning potential of lignin sulphonic acid and its derivatives which give many indications that these materials are a potential source of replacement tannins.[2]

Work was taken up at this Institute to investigate the problem of a better utilisation of locally available waste sulphite liquor, following one of the most suited type of chemical modifications, *viz.*, condensation of lignin sulphonic acid with other phenolic reagents. This type of modification is designed to improve the tanning potential of sulphite lye by increasing the hydrogen bonding loci of the lignin sulphonic acid in such a way that the product of condensation always remains water soluble. Special attention was paid to the water solubility of all the derivatives, as the tanning extracts that are used today, are water soluble materials and all tanning procedures and equipment are geared to an aqueous tannage.

Experimental

The commercial waste sulphite liquor used by us was supplied by M/s. India Paper Pulp Co. Ltd., Calcutta. This chiefly consists of the magnesium salt of lignin sulphonic acid with other particulars as follows :

1. Density = 50 Twdl.
2. pH = 7.5
3. Total solids = 72% by wt.
4. Ash = 9.5 % by wt.
5. Total sulphur = 6.6% by wt.
6. Sulphate sulphur = 0.33% by wt.
7. Sulphite sulphur = 0.40% p wt.
8. Organic sulphur = 5.9% by wt.

No attempt was made to remove the residual sugars etc., since the presence of small amounts of these during the tannage has not been considered detrimental.

A. Preparation of the Derivatives

I. Lignin sulphonic acid—Resorcinol condensate: Previous condensations of phenolic substances with lignin sulphonic acid appear to have been carried out under anhydrous conditions in the presence of an acid catalyst. In the first instance, a more commonly available polyphenol namely resorcinol, was condensed with magnesium lignin sulphonate in the presence of hydrochloric acid as catalyst. The condensate was found to be insoluble in water. This could, however, be rendered water soluble by treatment with sodium bisulphite. This additional processing required to impart water solubility to the modified lignin sulphonate would involve considerable additional cost which might render the process uneconomic. It was with this consideration that the magnesium lignosulphonate was converted to the sodium salt of lignosulphonic acid by treatment of the sulphite liquor with sodium carbonate. The sodium salt when condensed with resorcinol at 130°C. for 2 to 3 hours under reflux, in presence of hydrochloric acid as catalyst gave a water soluble derivative. This was further treated with comparatively smaller amount of sodium hydrosulphite in order to get a paler colour imparted to the leather tanned by it.

II. Lignin sulphonic acid—Phenol condensate: To carry out condensation with phenol, it was not necessary to maintain anhydrous conditions. Sulphite waste liquor was either decationised or brought to a pH within 0.7 to 1 by adding sulphuric acid and then refluxed with an equal amount by weight of phenol for 3 hours. The product of condensation was water soluble.

III. Lignin sulphonic acid—formaldehyde condensate: The phenolic hydroxyl groups of the lignin material are responsible for effecting a condensation of lignin sulphonic acid with formaldehyde. This was accomplished by refluxing the waste lye with formaldehyde for 3 hrs. under acid conditions.

IV. Phenol-formaldehyde—Lignin sulphonate derivative: This was prepared by condensing phenol and formaldehyde in the presence of waste sulphite lye under reflux. The temperature maintained throughout the reaction was 95°C. and the time required for the completion of the process was 3¼ hours.

V. Phenol/Cresol sulphonic—formaldehyde-lignin sulphonic acid derivative: Phenol or cresol separately or a blend of both were first sulphonated with an equal amount by weight of sulphuric acid at 100°C. for 6 to 7 hours. To this was added the lignin sulphonate of the waste sulphite lye, and both the sulphonic acids mixed thoroughly. The resulting mixture was then condensed with 30% formaldehyde at room temperature for 12 hours. To the thick condensed mass, a little urea solution was added dropwise under stirring, followed by further condensation with formaldehyde. Finally, the syntan prepared in the above manner, was neutralised with conc. sodium hydroxide solution to pH 2.5.

B. Preliminary evaluation of the tanning potential

In order to assess the combining power of the modified lignin sulphonic acid derivatives with the protein of the hide, preliminary experiments were carried out by precipitating gelatin from its solution, by the addition of an excess of tan solutions, and determining thereby the amount of tannin fixed in each case. In actual practice, one per cent gelatin solution was prepared and divided into five 20 c.c. portions in different beakers. All the tanning materials under investigation were separately dissolved in water to give tan solutions of 20°Bk. each, and the pH of these solutions adjusted to 2.5. 50 c.c. portions of each of these tan solutions were added to the gelatin solution in the beakers individually, the mixture stirred and the resulting precipitate allowed to settle for a while. The precipitate was washed thrice with 20 c.c. of water each time by decantation. The washed precipitates were stretched to thin films on petri-dishes and left overnight to dry. Next day, the apparently dried gelatin precipitates were further subjected to vacuum drying to ensure complete removal of moisture. The dry samples were then used for nitrogen estimation by Kjeldahl method and the amount of tannin fixed calculated.

C. Tanning Tests

Pieces, cut from the butt portion of a completely delimed goat skin were treated with tan solutions of 20°Bk. strength at pH of 4.5 until complete penetration. In all the cases, the tannins struck through the skin completely within 2 days. The strength of the tan solution was then raised to 30°Bk. and the pH adjusted to 2.8–3.0. The skin pieces were shaken in the solution for a few hours and then left immersed in the tan bath overnight. Next day, they were washed with small amounts of water, squeezed, slicked out, and finally oiled with pungam oil. The leather pieces were dried in shade and then staked. The properties of each leather piece are noted as shown in Table I.

Data and Discussion

The results of the tanning tests as well as the amount of tannin fixed by gelatin are given in the following Table with respect to the various derivatives obtained by condensing lignin-sulphonic acid with different phenolic substances.

TABLE I

S. No.	Tanning material	Leather feel	Colour	Shrinkage temperature	Amount of tannin fixed by gelatin
					PER CENT
I	Lignin sulphonic acid-resorcinol condensate	Excellent ...	Pale yellow	70°C	74.6
II	Lignin sulphonic acid-phenol condensate	Papery ...	Dull blackish	61°C	63.0
III	Lignin sulphonic acid-formaldehyde condensate	Rough ...	Dull yellow	66°C	61.4
IV	Phenol-formaldehyde-lignin sulphonate derivative	Bony ...	Do.	65°C	52.3
V	Phenol/cresol sulphonic-formaldehyde-lignin sulphonic acid derivative	Excellent ...	Light pink	70°C	89.2

The leather tanned by resorcinol–ligninsulphonic acid condensate was good in all respects except for slightly yellowish colour. Also, it is obvious from the values of tannin fixed by the gelatin that this material was second only to the derivative prepared by condensing phenol sulphonic and lignin sulphonic acids by means of formaldehyde. Nevertheless, it was considered important to investigate the possibility of using any other cheaper phenolic material in place of resorcinol. For, the comparatively high cost of resorcinol, which is available only from foreign sources at present, renders the product of condensation very uneconomical for making commercial leather. Moreover, the commonly available commercial phenol and cresols appeared to be more suitable for use, in view of their abundant local supply. Being the bye-products of the coal-tar industry, these materials are sufficiently cheap.

The reaction between phenol and lignin sulphonic acid could be effected in aqueous solution provided the waste liquor is previously decationised or brought to a pH value of 0.7 to 1.0 and as such, in all our experiments the waste liquor was treated with conc. H_2SO_4 to adjust the pH to the said range. The phenol condensate was, however, not found to be as good a tanning agent as the resorcinol one. The leather tanned by it was papery, though it had a smooth feel. The colour of the leather was also very objectionable. The ligninsulphonic acid was also condensed with formaldehyde with the expectation that the increase in its particle size may result in a better tanning agent. The tanning potentiality of the product obtained thus, though better than that of unmodified ligninsulphonic acid, did not yield satisfactory leather. The amount fixed by the gelatin is comparable to that in case of phenol condensate. Having found the products of phenol and formaldehyde condensation alone with lignin sulphonic acid unsatisfactory, it was considered worthwhile to utilise both of them together in single preparation. A preliminary study of such a process gave indications that comparatively much smaller quantities of phenol and formaldehyde could be condensed along with waste sulphite liquor as in process IV in order to get a completely soluble product. Higher quantities of phenol and formaldehyde when incorporated, resulted in the formation of resinous masses. The extent of modification of lignin material in this case was so little that the leather tanned by this material did not possess the qualities of a good leather. The combination of gelatin with this derivative was also poor.

On the basis of the experimental information stated above, it was felt necessary to sulphonate the phenol or cresol prior to the condensation with lignin sulphonic acid and formaldehyde so as to introduce comparatively larger quantities of each of these materials to yield a satisfactory replacement syntan. It was done so quite successfully as explained in process No. V. As is obvious from Table 1, the product obtained by this method was not only superior to the other phenol and formaldehyde condensates, but also had an advantage over the resorcinol derivative of lignin sulphonic acid in that it yielded light coloured leather with excellent feel and fullness. The fact that commercially impure phenol-cresol blend could also be utilised in place of pure phenol etc., was also established by carrying out a number of preparations with the former. The tensile strength as well as the tearing strength of the leather tanned by this material are given below :

Table 2

Test No.	Tensile strength (lb./sq. in.)	Elongation (Per cent)	Double Hole Stitch Tear strength (lb./inch)
1.	2310	50	245
2.	2592	50	340

Further work regarding the economics of the process and the possibility of a more successful application of this material to various tannages is in progress and the results will be published elsewhere.

ACKNOWLEDGEMENT

We shall fail in our duty if we do not thank Messrs. India Paper Pulp Co., Calcutta for providing us free samples of the sulphite waste liquor, and the Director, Central Leather Research Institute, for the interest shown in the investigation.

REFERENCES

1. Tu, S. and Lollar, R. M. : *J.A.L.C.A.*, 45, 324 (1950).
2. Lipsitz, P., Kremen, S. S. and Lollar, R. M. : *J.A.L.C.A.*, 44, 194 (1949).

Discussion

Dr. A. Seetharamiah : In our country, paper is manufactured from bamboo ; sulphite liquor may not be available in quantities adequate for manufacture of tanning materials. So the paper could be of only academic interest.

Mr. Mathur : Actually the problem has been suggested and initiated at the Institute by the paper mills only.

Dr. S. K. Barat : I wish to reiterate what Mr. Mathur has said. The investigation was made with another view also namely to throw some light on the hitherto unexplained ideas of vegetable tanning mechanism.

Prof. A. N. Mikhailov : Dr. Barat's idea of colorimetric analysis is very interesting. But I doubt if we can decolourise tannins. The colorimetric analysis of ligno sulphonates is an example of the usefulness of methods for evaluation of tannin extracts. Our tests have shown that Ts is not high enough and the leather formation is not very good.

Dr. S. K. Barat : While the Ts for all the products have not been determined the amounts of tannin fixed have been determined. I am only suggesting that if a suitable colorimetric method is available, the problem may be more easily tackled. Once the tanned polyamide is got, nitrogen could be determined with micro kjeldahl apparatus. If this is done with hide powder, ash content has to be taken into account. Determination of nitrogen in the polyamide would give directly the tannin fixed. The non-tannin fractions could then be determined by the official method.

FLAVOGALLOL—A CONSTITUENT OF THE TANNIN FROM POMEGRANATE RIND

BY

OTTO TH. SCHMIDT AND WERNER FICKERT
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ABSTRACT

Flavogallol, a sesqui-ellagic acid has been isolated from the products of acid hydrolysis of tannins from pomegranate rind.

SURVEY OF INDIGENOUS TANNING MATERIALS

Kahua bark (*Terminalia arjuna*)

BY

J. B. RAO, T. S. KRISHNAN AND Y. NAYUDAMMA

(*Central Leather Research Institute, Madras*)

ABSTRACT

Modification of the objectionable red colour which Arjun bark imparts to the leather, have been made by suitably blending it with *Cassia marginata* or konnam in E.I. tanning of hides. The properties of the tanned leathers like general appearance, colour, feel and other physical, chemical and microscopical characteristics of the leathers have been found to be comparable with those of the imported wattle tanned leathers. As it gives a firm leather of a very high degree of tannage, attempts are being made to utilise it in sole leather tannage. This bark is suitable for the preparation of extracts as it can easily be leached and the extract gives a high percentage of tannin.

Chairman's concluding remarks

The Chairman, in his concluding remarks, said that he would like to associate himself with the remarks made by Mr. Sanjoy Sen the previous day. However, he would be failing in his duty if he did not deal with the other side of the question. He would request the tanners to make use of this Research Institute, put their problems to them, and get their difficulties solved. The tanners should make full use of this Institute by co-operating with each other and by bringing problems to this Institute. It was to the credit of the Institute that it could attract a personage like Prof. Mikhailov to come and present a paper here.

Dr. E. C. Mathew proposed a vote of thanks.

PROCEEDINGS OF THE TECHNICAL SESSION IV

16-3-1958—*Afternoon*

Chairman : Dr. G. S. Laddha, Director, A.C. College of Technology, Madras.
Recorder : Mr. R. Selvarangan.

Dr. S. K. Barat, Central Leather Research Institute introduced the Chairman.

After initiation of the Session by the Chairman, papers were read in the following order :—

Synthetic products for leather greasing and fatliquoring — Composition properties and application.	Read by Dr. N. R. Rao, Fedco Ltd., Bombay.
Petroleum products for the leather in industry.	Read by Mr. T. V. Jagadeesan of Stanvac Ltd., Madras.
Surface active materials as auxiliaries in leather industries. Emulsifiers for use in leather industry.	Summary given by Mr. V. R. Kishore and amplified by Mr. M. A. Ghani.
Unit process of sulphonation.	Presented by Mr. K. Chandrasekharan
Sulphated oils prepared at the Central Leather Research Institute and their use in leather.	Gist given by Mr. V. V. Murlidhara Rao.
Indigenous fish oil for the tanner.	Read by Mr. G. P. Madhavan.
Use of sugarcane wax in leather polishing.	Read by Mr. V. V. Mhaskar.
Sugarcane wax for shoe polishes. Natural latex based adhesive for leather.	Presented by Mr. G. S. Rama Iyer.
Coated abrasives in leather and shoe industries.	Read by Mr. U. Mohan Rao.
A comparative study of the mechanical properties of chrome retanned upper leathers.	Presented by Dr. N. Ramanathan.
The application of quality control to leather research in industry.	Read by Mr. S. Venkataraman.
Cationic, nonionic and multi-charged fatliquors.	Taken as read.

SYNTHETIC PRODUCTS FOR LEATHER GREASING AND FATLIQUORING—COMPOSITION, PROPERTIES AND APPLICATION

BY

H. GRUNEWALD

(*Farbwerke Hoechst A.G., Hoechst*)

ABSTRACT

The composition, properties and applications of the Derminol products, used for leather greasing and fatliquoring are discussed in a detailed manner.

Greasing and fat-liquoring is a very important phase in the production of leather. There is hardly a type of leather whose specific properties do not depend on the proper application of fatty materials.

A review of the development of leather greasing in the last decades shows the important modifications effected in this section of leather production, by taking advantage of chemical findings and new working techniques.

Up to 50 years ago the water-insoluble oils and fats were used alone. The development of chrome-tanning led to the technique of fat-liquoring, soap and egg yolk being the first emulsifiers for natural oils. The known drawbacks of such soap emulsions—alkaline reaction, sensitivity to acids and hard water—could be removed by using sulphonated oils. In the years after 1920, the chemical industry developed new auxiliaries for leather stuffing which were obtained by the chemical treatment of natural products, for instance the known alkylsulphates of fat and the condensation products of fatty acids. As a result of extensive research work, synthetic leather greasing materials on a purely synthetic basis have been elaborated in Farbwerke Hoechst AG, during the last 15 years known under the name " Derminol "* These products have given good results and are today valuable auxiliaries in the leather manufacture. They have got their importance besides the natural fats and have proved suitable in many cases to obtain greasing effects which cannot be reached with natural products.

I. Composition of synthetic greasing materials for leather

The basis for the production of Derminol products, paraffin-hydrocarbons, with unbranched straight chains, are obtained by the *Fischer-Tropsch process*. In this process water-gas, *i.e.*, a mixture of carbonoxide and hydrogen obtained by treating red hot coke with water, is warmed up to temperatures of 200 to 270°C in the presence of catalysts, at normal pressure.

A certain fraction of these Fischer-Tropsch paraffin-hydrocarbons, known under the designation *Kogasin* † is utilised for preparing the leather greasing agents. Kogasin which contains a small portion of unsaturated hydrocarbons is converted into *Mepasin* by hydrogenation, to constitute *saturated* hydrocarbons.

The subsequent treatment of the Fischer-Tropsch-hydrocarbons is different depending on the type to be produced—leather oils, leather fats or fat liquors. These three different types of leather stuffing agents can be manufactured on this basis.

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* Registered trademark.

† Registered trademark.

For producing *leather oils*, as for instance Derminol Oil H/F or Derminol Grain Oil HG, a certain fraction of Mepasin with a chain length of C_{10} to C_{20} is treated with chlorine, by which chlorine is substituted for hydrogen. The viscosity of the oils can be influenced by varying the chlorine content of the chlorinated hydrocarbons obtained ; a higher chlorine content results in a higher viscosity. The chlorine content of the leather oils of the trade is about 30 to 40 percent. A chlorine content of 41 percent and a chain length of C_{15} results in an average composition of $C_{15}H_{22}Cl_4$.

By treating selected wax-like fractions of the Fischer-Tropsch synthesis having a higher melting point with chlorine, it is possible to produce *leather fats* which, as for instance *Derminol Fat HK*, have found much application, especially in the stuffing of vegetable-tanned leather instead of tallow. These higher molecular chlorinated paraffins contain about 6 to 12% chlorine and are distinguished—even in combination with Derminol oils of low viscosity—by an excellent penetrating power and a good bond in the leather.

While the processes described so far have resulted in water-insoluble oils and fats for the leather treatment, in the following, the method of manufacturing water soluble products, that is *fat liquors*, will now be described. Mepasin is the basis to start from. By the familiar Reed sulphochlorinating process, sulphur dioxide and chlorine are under the influence of ultra-violet light made to act simultaneously on Mepasin. Mepasin sulphur chloride is obtained and is known under the name *Mersol* *. With certain modifications it has been introduced in the trade under the name *Immergan.** Mersol is converted with ammonia into sulphamide and then with chloroacetic acid into sulphamido acetic acid. This Mepasin sulphamido acetic acid is the main constituent of the first fully synthetic fat liquor, the Derminol Liquor 1.

It is comprehensible that by varying the described reaction, manifold variations can be realised for the manufacture of differently modified synthetic fat liquors. The properties of the fat liquors thus obtained can be influenced in many ways, by causing the Mepasin sulpho chloride to react with other compounds capable of reaction, for instance, amines, amino-sulphonic acids, aminocarbonic acids, etc. In this way it is possible to define the emulsifying power, the particle size, the direction of charge, the wetting power, the water-repellent properties and many other characteristics. Thus, the product obtained can be adapted to all desired applications.

II. Properties of the Derminol products

Derminol oils and Derminol fats and particularly Derminol liquors have gained a permanent position in the range of leather-stuffing agents. The special properties of synthetic leather-stuffing agents shall be discussed now, stressing thereby their differences from and advantages over the natural fatty substances.

The naturally occurring fats and oils of animal and vegetable origin, such as tallow, cod-oil, sperm oil, olive oil, etc., are essentially glyceric esters of higher fatty acids. Sperm oil contains, in addition to these esters, a considerable portion of fatty alcohol esters of higher fatty acids. The glyceric esters of natural fats and oils are hydrolysable by diluted acids and alkalies, under the influence of humidity and heat as well as by bacteria and mould fungi, for which the natural oils and fats present a good culture medium. From these esters, besides glycerine, different fatty acids are obtained, these fatty acids, consisting of both solid (palmitic acid, stearic acid), and fluid (oleic acid, linoleic acid) acids. Solid fatty acids have a stronger tendency to crystallize than their glycerides and are the main cause for the formation of white fatty spues on leather.

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* Registered trademark.

One of the most important fatty acids of cod oil, the C_{22} hexaenic acid is a strongly unsaturated fatty acid with 6 double bonds. Such fatty acids with several unsaturated double bonds, another instance of which is the linoleic acid contained also in the cod oil, tend to get oxidized and to produce a resinous spue on leathers treated with cod oil.

Such chemical alterations leading to the secretion of crystalline fatty acids or exudation of resinous oxidation products of cod oil occur not only in the case of untreated natural oils but also to a greater extent still with chemically modified natural fats, such as sulphonated cod oils. Partial splitting of the glyceric esters takes place generally during the sulphonation, so that free fatty acids are thus liable to be secreted when sulphonated oils are used in fat liquor.

With regard to their properties the synthetic leather-stuffing agents based on chlorinated hydrocarbons differ from natural oils and fats by the fact that they are not esters, do not contain free fatty acids and are attacked neither by bacteria nor by mould fungi. These properties have a favourable effect on the leathers treated with Derminol stuffing agents. Fatty or resinous exudations which may occur by hydrolytic splitting and oxidation of fats do not occur when Derminol greasing agents are used alone. The simultaneous use of Derminol products reduces the tendency for secretion in leathers which are treated with natural fatty materials or which contain natural fat from the raw hide. This spue preventing effect is due to various reasons :

(1) The synthetic greasing agents cannot be split hydrolytically and therefore do not lead to formation of crystalline fatty acid exudations.

(2) The chlorinated hydrocarbons have a dissolving power for fatty acid secretions derived from natural fat, so that those secretions cannot appear in crystalline form. Even resinous ploymerization products of unsaturated fatty acids are dissolved.

(3) The Derminol greasing agents prevent mould growth on the leathers as they present no culture medium for micro-organisms.

Experience of many years has shown that the formation of spue on finished leathers could be prevented in many leather factories by the simultaneous use of Derminol greasing agents.

Many natural oils, particularly fish oils, are not fast to light and oxidation. This is due to the fact that on the one hand, leathers greased with such natural fats have the tendency to become yellow and that on the other hand, the quality of such natural products is subject to strong variations, as can be recognized by large differences in the analytical data. Owing to the influence of atmospheric oxygen on the fish oils their colour and viscosity can change to a large extent, so that for instance a cod oil which when fresh, is quite suitable for oiling leathers and shows a high penetration power, loses, after prolonged storage, in consequence of an increased viscosity, this quality, penetrating only very badly and producing absolutely different greasing effects. In contrast to this, the synthetic Derminol products, which can be used instead of cod oil, neat's foot oil or sperm oil are absolutely uniform and stable even after a prolonged storage time ; their natural colour is paler than that of the most natural oils ; no oxidation is possible as the products have no unsaturated portions ; the Derminol greasing agents have therefore an excellent fastness to light and are particularly suitable for pale and white leathers, even for reptile leathers. Changes of viscosity during the storage time are excluded, so that these products can be utilised always in the same way, and uniform results are to be expected in the stuffing operation.

Recently, cheap mineral oils are often used simultaneously for leather greasing. Though giving a relatively good softening effect, these oils have the drawback that they are not firmly bound in the leather and can be easily washed out. The utility of such leathers greased with mineral oils, rapidly decreases in rainy weather or snow ; after drying, these leathers become hard and stiff. When applying mineral oils their lack of affinity for the leather fibre should always be taken into account and therefore the fraction of mineral oil admixed should be kept as low as possible or even dropped. The bad fixing of mineral oil to the leather accounts, as is known, also for the marking off of the leather treated with it. Difficulties resulting in the dressing, especially in the collodion dressing of these leathers are due to the migration of mineral oil fractions. Contrary to this the *Derminol greasing agents* have a pronounced good affinity for the leather owing to their chlorine content. This was confirmed by the very hard strain to which the leathers finished with Derminols were exposed.

Special attention should be given to the emulsifiability of the water-insoluble Derminol oils as well as to the emulsifying power of the Derminol liquor brands. As will still be shown later on, Derminol oils are more easily emulsified than natural oils, as for instance neat's foot oil or castor oil. The distribution of fat obtained by the simultaneous use of Derminol oils, even if these are combined with certain fractions of natural oils, is considerably finer than when using neat's foot oil, sperm oil, etc., alone. The high specific gravity of the chlorinated hydrocarbons (>1), accounts for this good property. On mixing Derminol oils of a specific gravity >1 to and natural oils of a specific gravity <1 oil mixtures are obtained whose average specific gravity is nearly 1.0. Such mixtures are more easily emulsified and yield emulsions of better stability than the specifically light natural oils alone. The properties of the Derminol greasing agents, mentioned so far, apply to all Derminol products, *i.e.*, for Derminol oils, Derminol fats and Derminol liquors. The individual products will now be discussed with regard to their particular fields of application. (*See* Table 1, Page 155.)

1. Derminol oils

There are on the market 2 synthetic water-insoluble leather oils, *Derminol Grain Oil HG* and *Derminol Oil H1F*, which differ from each other by their chlorination grade and therefore by their viscosity. Derminol Grain Oil HG is the oil of a low degree of chlorination and a lower viscosity, Derminol Oil H1F is higher chlorinated and has a higher viscosity. Both products are miscible with all natural greases and mineral oils as well as with Derminol Fat HK. The less viscous Derminol Grain Oil HG is primarily used for oiling the grain of sole leathers as well as very often for oiling uppers replacing thereby the kid finish oil. Due to its low and non-varying viscosity it penetrates well into the grain, is finely distributed and increases the water-repellent effect of vegetable-tanned leathers. It is comparable in its action to oiling with a good clear cod oil of low viscosity ; however, it has the advantage of a better stability and has a clearing effect on the colour of vegetable-tanned leathers. Derminol Oil H1F with the higher viscosity is especially used for stuffing the different leather kinds, such as russet uppers, harness, welting, and belting as well as waterproof leathers ; it is utilised in combination with

TABLE 1

Derminol Products		
Water insoluble		Water soluble
Derminol Grain Oil HG. Derminol Oil H1F.	Derminol Fat HK.	Derminol Liquor AS Derminol Liquor EMB. Derminol Fur Liquor HSP. Derminol HLW.

other fat materials, such as cod oil, Derminol Fat HK, tallow, and degras. A further field of application is the replacement of high-grade natural oils, particularly of neat's foot oil, in liquors for treatment of uppers. In such liquors, neat's foot oil can be entirely or partly replaced by Derminol Oil H1F. This synthetic leather oil gives more finely dispersed and more stable emulsions than neat's foot oil. A remarkable advantage of the admixture of Derminol Oil H1F is, however, its capability of counteracting spue and bacteria growth.

2. Derminol Fat HK

Derminol Fat HK is used as the solid component in stuffing mixtures for vegetable-tanned leather, such as russet uppers and harness leather as well as for waterproof leather produced in combination tannage. It has tallow-like consistency. It has the advantages of not crystallising and not becoming rancid or hydrolysed. Fat exudations and mould growth are not likely to occur when it is used alone. When admixed, its mould preventing effect grows in the order as its proportion in the mixture increases. Derminol Fat HK is compatible with all water-insoluble natural oils and natural fats, also with degras as well as with mineral oils and can moreover be used in emulsion fat liquors in combination with synthetic liquors.

3. Derminol liquors

Starting from the experience gathered with Derminol Liquor 1, various types of synthetic leather liquors which can be diluted with water have been developed the last years. The most important of them are the brands Derminol Liquors AS and EMB, and Derminol Fur Liquor HSP.

Derminol Liquor AS is a clear, brown liquid which is distinguished by an excellent emulsifying power for water-insoluble oils. It gives a deeply penetrating greasing effect with dry handle. It is preferably applied where a soft and dry greasing is requested, as for instance on suede leather, clothing leather, soft uppers, etc. Combined with other water-insoluble and even water-soluble greasing agents it can be successfully utilized also for all other types of leather, its emulsifying power permitting the simultaneous use of high amounts of water-insoluble oils. The stability of the emulsions and thereby the uniform fat distribution in the leather can remarkably be improved by the use of Derminol Liquor AS.

Derminol Liquor EMB : Shows a very high emulsifying power for oils and fats. It penetrates less deeply into the inner layers of the leather ; this fact, is of importance for chrome uppers which should have a higher firmness and a somewhat greasy surface. Derminol Liquor EMB confers to such leathers the desired elasticity. It is capable of converting even high amounts of tallow and higher-melting fats into sufficiently stable emulsions and is therefore suitable for the liquoring and stuffings of vegetable-tanned leathers. Due to its chemical composition it confers a certain amount of water-repellancy to chrome-tanned leather. It has proved particularly suitable for leathers dried by the Pasting Process.

Derminol Fur Liquor HSP was originally developed for the dressing of furs. It renders good services in the stuffing of glove kid, clothing leather and other types of leathers which are required to turn out very soft. It can be utilised in the place of egg yolk. This liquor has a strikingly high fastness to chrome, acid and salt which allows its application in the mineral tanning process. Derminol Fur Liquor HSP can, in this case, be added directly to the chrome liquor in the same way as a cationic product.

After having dealt with the different brands of the Derminol range, the most important application of Derminol products, namely in fat liquors, will now be discussed.

With knowledge about the properties of the different liquors and about the possibility of influencing the charge and the particle size of fat emulsions it is possible to control and guide the distribution of fat in the leather, influencing thereby in the desired way the character of the different types of leather. This control is possible with fully natural products only to a certain extent. The above mentioned possibility of widely varying the production of synthetic greasing agents makes it much easier to influence the kind and character of the desired emulsions. Fat liquors are colloidal systems which mostly contain water-insoluble fractions that are kept in very fine dispersion by means of emulsifiers. Depending on the composition of these emulsifiers one distinguishes between anionic, cationic or non-ionic emulsions. The charge of such emulsions determines their different behaviour towards the various leather types. Anionic liquors give generally, on cationic chrome leather a relatively superficial greasing, while on anionic vegetable-tanned leather they effect a deep penetration. On the other hand cationic liquors are deeper penetrating in chrome leather than most of the anionic liquors. Non-ionic liquor emulsions are only little influenced by the charge of the leather and yield mostly a good penetration of the fat substance unless—as in the case of many vegetable-tanned leathers—the non-ionic emulsifiers lose their effectiveness by their reacting with the vegetable tannins.

As to the character of the charge of our Derminol liquors it may be mentioned that these liquors contain anionic components ; however, the brand Derminol Fur Liquor HSP has certain characteristics of the cationic emulsions and brings about a good penetration of the fatty substance into chrome leather. Derminol Fur Liquor HSP is outstanding for its high fastness to acids, chrome and electrolytes. It can therefore be used simultaneously with mineral tannins and in high salt concentrations.

TABLE 2

Emulsifying power of Derminol liquors alone and in mixture with sulphonated oils for various oils, oil mixtures and fats

Derminol liquor	AS	HSP	EMB	AS+sulph. cod oil 1 : 1	AS+sulph. neat's foot oil 1 : 1
Derminol Oil H1F	45	65	100	120	120
Derminol Grain Oil HG.	65	95	70	120	120
Mineral Oil	120	230	25	140	300
Sperm Oil	25	45	120	40	50
Cod Oil	17	35	100	30	60
Neat's foot oil	7	25	100	30	40
Derminol Oil H1F + Neat's foot oil.	25	25	125	80	80
Peanut Oil	7	30	100	...	...
Wool grease	100	300	230	...	...
Derminol Fat HK	2	12	170	...	...
Tallow	25	55	230	...	...

The percentage figures indicate the approximate maximum quantities of oil and fat which can be converted into stable emulsions by 100 parts of the respective liquors within 24 hours without creaming up. In practical working a shorter stability than for 24 hours suffices in most cases, so that in general amounts of oils higher than those indicated above can be converted into sufficiently stable emulsions.

It is seen from this Table that Derminol Liquor AS has a good emulsifying power for sperm oil and cod oil and that it is able to emulsify very high amounts of Derminol oils and mineral oils. 25 per cent of a mixture of neat's foot oil and Derminol oil H1F is converted into a stable emulsion by the addition of Derminol Liquor AS.

Derminol Liquor EMB shows a strikingly high emulsifying power for unsulphonated natural oils. It can be mixed with equal amounts of unsulphonated cod oil, neat's foot oil and sperm oil and more than 200% of wool grease or tallow. Even paraffin and stearine can be emulsified. After thinning, emulsions are obtained which are stable for 24 hours without creaming up.

It is a striking observation that by combining Derminol Liquor AS with sulphonated oils, for instance sulphonated cod oil or sulphonated neat's foot oil, the emulsifying power for different unsulphonated oils and mineral oils can considerably be enhanced beyond that of the individual liquor components.

It is surprising that a certain high-graded sulphonated cod oil shows only a very low emulsifying power for natural oils admixed, but that this emulsifying power is considerably increased by the addition of 10 to 20% of Derminol Liquor EMB or AS and rises still with increasing additions up to a maximum that differs for the various oils and the different mixing ratios.

There are of course differences in the emulsifiability of the various cod oil types as well as of other natural oils which must be determined in each case. It may be mentioned that Derminol Liquor EMB has in general a better emulsifying power than Derminol Liquor AS for types of cod oils which are difficult to emulsify.

It may be mentioned that it is possible to emulsify natural oils with small amounts of highly effective emulsifiers, as for instance alkylsulphates of fat, condensation products of fatty acids and condensation products of ethylene oxide. Such emulsions may be very stable, but have, as compared with those prepared with the aid of our synthetic Derminol liquors the drawback that the leathers treated with them have a very high wetting power and absorb much water. These emulsifiers are mostly products which are not only emulsifiers but also wetting agents, whereas we have used for the development of our Derminol liquors, chemical substances which though having an outstanding emulsifying power have only a low wetting power. In addition, they are not only emulsifiers but also to the same degree greasing agents thanks to their high content of water-repellant hydrocarbon radicals.

III. Application

Finally a number of examples of application of our Derminol greasing agents shall be mentioned, which in practice of long years have given good results.

For the preparation of liquor emulsions it is advisable to stir the whole amount of oil to be emulsified in the undiluted liquor and to continue the agitation until a perfectly homogeneous mixture is obtained. Water of about 70°C is added in small portions with stirring which is continued until the emulsion is uniform ; only then the bulk of the water is added. It is not advisable to boil up the stock emulsion by introducing steam as in this case the very fine distribution of the grease in the emulsion could be interfered.

On emulsifying solid fats, as *e.g.* tallow, paraffin, stearine, wool grease, Derminol Fat etc., the solid fats are first melted, then the Derminol Liquor is stirred into this melt and the whole emulsified with water at about 70°C. according to the above mentioned method.

As a general rule of application a partial replacement of sulphonated fat liquors as well as of water-insoluble oils by Derminol greasing agents gives more stable emulsions, a considerably improved greasing effect and a smoother run of the working process. It is therefore possible to replace in the existing recipes, half the amounts of sulphonated cod oil, sulphonated neat's foot oil or sulphonated sperm oil by Derminol Liquor AS, EMB, or Derminol Fur Liquor HSP and to substitute our Derminol Oil H1F for one part of the neat's foot oil or cod oil applied.

When stuffing willow sides which are to be pasted, surface stuffing as well as a good penetration of the fat are generally requested. The elasticity of the grain and the adhesive effect shall thus be improved. For this purpose, the combined use of anionic fat-liquoring agents and cationic fatty substances in separate baths is often recommended. With Derminol Liquors it is, however, possible to liquor in one bath. At first, a well penetrating liquor on the basis of Derminol Liquor AS is *e.g.*, used and then a fat emulsion of low stability based on Derminol Liquor EMB and larger quantities of unsulphonated oils is added to the exhausted liquor-bath. The process is carried out as follows:

First Liquor: 1.0% Derminol Liquor AS, 0.5% Derminol Liquor EMB and 0.5% Derminol Oil H1F.

Addition to the same bath: 1.0% Derminol Liquor EMB, 1.0% unsulphonated fish oil or sperm oil and 0.5% Derminol Oil H1F.

Leathers which are sufficiently smooth already from the tanning process, as, *e.g.*, uppers which have undergone a relatively intensive vegetable after-tanning, require only one stuffing bath, *e.g.*, with 3.0% Derminol Liquor EMB and 2.5% unsulphonated sperm oil for obtaining favourable results.

Derminol Liquor AS is particularly suitable for the stuffing of suede or velvet leathers with the usual short nap. A good penetration of the fat, a satisfactory softening effect, as well as a short and dry handle are obtained without overfatting the fibre. For calf velvets, *e.g.*, 1.5—2.0% Derminol Liquor AS, 1.0% Derminol Liquor AS, 0.5% unsulphonated castor oil, 1.0% egg yolk and 1.0% Romolgan HA * (a non-ionic rewetting agent) are used. Velvet leathers intermediately dried are afterstuffed in the extracted dyebath with 1-2% Derminol Liquor AS. Recently, velvet leathers with somewhat longer fibres and a certain gloss effect are required. Such leathers are most suitably fat-liquored with Derminol Liquor EMB, Derminol Liquor AS, Derminol HLW, adding subsequently a small amount of degras; after neutralization, 1.5% Derminol Liquor EMB, 1% Derminol HLW or Derminol Liquor AS and 0.5% degras are used.

The dyed leathers are stuffed as follows: 1.5% Derminol Liquor AS, 1% Derminol Liquor EMB, 0.75% Derminol HLW and 0.75% Degras. These leathers can readily be buffed, if this treatment should be required. Leathers with long fibres showing a glossy two-way shine are obtained.

The development of fashion prefers recently very soft uppers, the so-called softy leathers. Such hides as will be worked up to mocassins, will be submitted even in the limehouse to a more intensive liming, thus preparing for the production of a very soft leather. The additional use of well penetrating and softening fat-liquoring agents, such as Derminol Liquor AS are recommended for the stuffing.

Neutralized cow hides are retanned with 5—10% of a synthetic tannin, as *e.g.* Coralon GP* or a vegetable tanning agent, as *e.g.*, mimosa extract. The leathers are then dyed. The fat mixture consisting of 4-6% Derminol Liquor AS, 1% Derminol HLW and 2-3% sulphonated sperm oil is added to the dyebath.

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* Registered trademark.

After a 60 minutes run, the bath is extracted with 4% formic acid. A very soft leather with a dry handle and a solid grain is obtained.

Football leather and other intensely stuffed leather types are mostly stuffed in the drum or on the table. When using Derminol Liquor EMB it is, however, possible to stuff these leathers also in a liquoring process. Owing to its very high emulsifying capacity, Derminol Liquor EMB enables the solid fats to penetrate into the leather in the form of liquors. The leathers obtained by this method show a very uniform distribution of the fat. The risk of stain formation is considerably reduced and the shade of such leathers remains very uniform. Football leathers are liquored with an emulsion containing : 4% Derminol Liquor EMB, 2% Stearine, 2% Paraffin, 0.2% ammonia tech. (25%) and 100 % water at 70°C.

After 45 minutes, the fat is well absorbed.

Leathers treated with a mixture consisting of 4% Derminol Liquor EMB, 4% wool grease and in 100% water show a good water-repellent effect.

When stuffing vegetable-tanned leathers, as for example, russet uppers and harness leather, the process of emulsion stuffing is more and more applied. Instead of stuffing with water-insoluble fat mixtures in the hot-air drum, moderately stable aqueous emulsions of water-insoluble fats are utilized in this process. A more uniform absorption, a faster exhaustion of the bath and purer leathers are obtained on which better dyeings will be produced. Derminol Liquor EMB is particularly suitable for the preparation of such emulsion stuffings. The following mixture is applied to harness leather and welting leather : 35 parts of beef tallow, 15 parts of sulphonated tallow, 20 parts of fish oil, 20 parts of Derminol Oil H1F and 10 parts of Derminol Liquor EMB. About 6-10% of this mixture is employed. This fat mixture is thoroughly stirred with the same amount of water and then introduced into the drum. It is absorbed by the leather within 45-60 minutes.

These recipes are only a few examples of the wide range of applications for which Derminol fat-liquoring agents may be used. Further details on the stuffing of the different types of leather are contained in our special leaflets.

By an intimate knowledge of the properties of the synthetic stuffing agents, of the many possibilities practicable through changing the liquor, the particle size of the emulsions and the ratio between emulsifying and emulsified portion in the liquor, it is relatively easy to obtain the desired stuffing effect for every type of leather. The results obtained in practice have confirmed that the synthetic Derminol liquoring agents are a valuable supplement to the natural stuffing agents for the treatment of all types of leather. They enable a better control of the stuffing process.

PETROLEUM PRODUCTS FOR THE LEATHER INDUSTRY

BY

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ABSTRACT

The petroleum products are characterised by high degree of penetration, better lubricating properties, nonoxidisability and chemical inertness. By using blends of these products with fatty oils, burning of leather, spue formation and loose grain are eliminated and the leather produced has greater firmness and is more waterproof. Thus petroleum products are vital auxiliaries in the production of high quality leather. The scope of utilisation of these products is indicated in this article.

The leather industry in India is the largest industry after textiles. The impetus given to the manufacture of high quality leather in this country has opened up prospects for commercial utilisation of petroleum products in the various manufacturing processes in leather making.

In the past, India exported, and still continues to export, considerable quantities of partially tanned hides and skins but the possibilities of manufacturing the higher quality finished leathers in India itself are being realised. Production of quality goods at competitive rates depends to a great extent on the efficiency of chemical processes in tanning and petroleum products have come to play a significant role in materially assisting such development.

Petroleum products which are used in the manufacture of leather include paraffinic and naphthenic base oils, paraffin wax, microcrystalline waxes, synthetic petroleum resins and certain petroleum sulphonated derivatives. All these products are selected and used on the basis of experience in their applications to the diversified requirements of tanning processes.

The suitability of petroleum oils for this purpose cannot be solely correlated to the conventional physical tests and experience has shown that the mere identity of two oils in terms of their usual tests is no assurance of comparable results in leather treatment. Generally speaking, paraffinic oils are preferable to naphthenic base oils because of their greater stability as well as their comparative uniformity in respect of such characteristics as interfacial tension. However, where emulsibility or emulsion stability are important considerations, naphthenic base oils are to be preferred.

Petroleum leather oils, apart from their lubricating value, promote penetration and because of their chemical inertness and resistance to bacterial action, provide a degree of stability and protection against deterioration not obtainable with straight fatty oils and greases.

Before petroleum products were introduced for treatment of leather, fatty oils were used exclusively. The idea of combining petroleum products with fatty oils to take advantage of natural lubricating, penetrating and keeping properties that petroleum products possess was a later development. The fundamental advantages of using petroleum based leather oils are as follows.

High penetrating properties : The unusual fluidity and spreading properties of petroleum products give them great penetrating and distribution properties, these being especially true of solid petroleum products, which change, when molten, to free flowing liquids that are more mobile than either tallow or stearine. For this reason blends of petroleum products and fatty oils have much better penetrating properties than fatty oils or greases alone. However, correct blending is essential to promote interfacial tension properties, to ensure thorough and uniform distribution over fiber surfaces and thus permit full development of physical characteristics for each type of leather. As a result of this uniform distribution, the leather takes on a better colour and a cleaner surface, and the thorough permeation of every fiber with oil or grease greatly increases the pliability and tensile strength of the leather.

Elimination of heating : Petroleum products are non-oxidisable and their presence makes the blends non drying or slow drying. The use of such products therefore prevents overheating and burning of leather in the mill or when piled.

Greater firming properties : Fatty oils and greases when used alone in currying mixtures have a marked tendency to produce flabby leather and to sweat out from the leather. By combining petroleum products in varying proportions with such materials, it is possible to give character and a degree of firmness that is not obtainable with fatty oils and greases alone.

Superior water proofing : The use of fatty oils alone for waterproofing of leather is unsatisfactory because they tend to emulsify with water and absorb it. This is particularly true if acids or alkalies are present, even in small amounts. Petroleum products, on the other hand, are highly resistant to the action of water whether or not acids and alkalies are present.

Stability of products : Petroleum products are characterised by their remarkable inertness and excellent keeping qualities. They are absolutely unaffected by atmospheric conditions and unaltered by majority of chemicals and also possess definite bactericidal properties. Since bacterial action is the cause for rancidity and deterioration of fatty oils, the presence of petroleum in mixture with such fatty oils effectively prevents rancidity by retarding bacterial activity. As a consequence, due to the stabilising action of petroleum, such blends practically never turn rancid and keep indefinitely both in the container and in the leather. Also, the free acid content in such products is held to a harmless minimum. Such great stability assures the tanner of effective currying materials even after protracted storage.

Elimination of spue and weak fibres and loose grains : Petroleum products are naturally inhibitors of spue of either the gummy or the powdery white type which frequently result from the use of fatty oils and greases alone.

This property is due to their not containing any spue forming bodies and petroleum also acts as a good solvent for such bodies occurring in fatty oils and greases.

Permanent lubrication of fibres : Without the stabilising influence of petroleum content, there is always the danger of decomposition of fatty oils and greases leading to impairment of lubrication and consequent loss of pliability and tensile strength of the leather. Accredited research organisations associated with the leather industry opine that the stability of petroleum products warrants their use to a maximum degree, compatible with the required firmness characteristics of the leather.

Type of petroleum based leather auxiliaries

Petroleum based leather auxiliaries can be classified into four general groups as follows :

1. Curriers' greases,

2. Leather specialities including petroleum based fat liquor compositions.
3. Compounded leather oils.
4. Straight petroleum oils.

The uses of these products are so diversified and subject to the varying practices of different tanners that it is not practicable to undertake a detailed or specific description. The following information is therefore confined to a statement of general uses.

Curriers' greases : These are combinations of white crude scale waxes and natural fats and are used in the currying of heavy leathers such as beltings, harness, army boot and mechanical leathers. In the currying process, these products are introduced in the leather in a molten condition by impregnation.

Fat-Liquor formulations : Petroleum products for fat liquor formulations are water soluble oils and are used in the fat liquoring of a wide variety oı light leathers such as dress, shoe, garment and glove leathers. These are made by blending highly refined and carefully selected mineral base oils with petroleum sulphonates of suitable molecular weights. Petroleum sulphonates are a prime requisite in the manufacture of petroleum based fat liquors and possess a good tolerance for alkaline earth salts. They act as powerful emulsifying agents for the mineral and fatty oils used in fat liquor formulations and assist in thorough penetration of the fat liquor into the leather fibres to assure suppleness and nourishment to the treated leather.

Compounded leather oils : Compounded leather oils and straight leather oils are used in the 'Oiling Off' process. Petroleum oils compounded with vegetable or animal oils are used in the so called wet oiling process and are applied to the grain surface of the dampened leather to supplement fat liquoring or currying treatment. This also protects the leather from oxidation and discolouration during the drying process and protects the leather from abrasive wear in service. Straight leather oils are primarily used in Finish Oiling process. The grain surface of finished dry leathers may be treated with a light application of this oil to supply additional lubrication, protect the leather from the vagaries of climatic changes and prevent the skins from sticking together when wrapped in bundles for storage or shipment.

In addition, the petroleum industry offers to the tanners, synthetic petroleum based fungicides, insecticides, water proofing resins, waxes, degreasing fluids, synthetic wetting agents and a host of other leather auxiliaries.

Discussion

Mr. S. C. Nandy (C.L.R.I.) : Is there any product to avert the fat adhering to the raw hide becoming rancid during the post-mortem period ?

Mr. Jagadeesan : A product to prevent halophilic bacterial effects had not been tried. However, there was a fungicide, which could stop the growth of red stains on hide.

Mr. V. R. Kishore (C.L.R.I.) : Is it possible to use mineral oils alone ?

Mr. Jagadeesan : If mineral oils alone are used, the leather produced will be brittle. So they are used only in admixture with the vegetable oils.

Chairman : What would be the length of the hydrocarbon chains in the case of the mineral oils suggested ? What should be the optimum length of the chain to get best results ?

Mr. Jagadeesan : Suitability of petroleum oils cannot be correlated with physical tests, molecular weight or hydrocarbon chain length. The effect of these on properties of leather like pliability, firmness, etc., is only a matter of conjecture.

Mr. G. S. Rama Iyer (C.L.R.I.) : To what extent are tetraline, decalin and paraffin wax melting point 50–52°C available in India and what are the prices?

Mr. Jagadeesan : Tetraline and decalin are not available. If the exact composition were given, suitable substitutes could be suggested. Paraffin wax is available.

SURFACE ACTIVE MATERIALS AS AUXILIARIES IN LEATHER INDUSTRY

BY

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ABSTRACT

The authors after describing the characteristics of the different types of surface active materials give details of the various operations where these materials find use in the leather industry, not only in processing of leathers but also in the fabrication of leathers and leather byproducts.

Introduction

In every industry, water plays an important role. Tanning trade is no exception as water has to be used in every stage of processing. Problems arise, when attempts are made to mix water with materials which it normally repels. Since water is incompatible with many materials, we have to seek a matter which will serve as a " go between " having affinity on the one hand with water and on the other with the dissimilar material. These " go between " substances are called surface active agents. The use of surface active agents is not limited to aqueous systems alone but since water is so widely used, surface chemistry pertaining to water has always been given more attention than non-aqueous systems.

Characteristics

Nature of surface active agents : Surface activity will result from the combination of a strongly polar group which is attracted to water (hydrophilic) and a non-polar group (hydrophobic) which is attracted to non-aqueous materials.

Most of the materials exhibiting surface activity are by nature, electrolytes, dissociating into ions in aqueous solutions. If one of the ions has hydrophobic characteristics, a surface active agent results. If the anion has the characteristics, the agent is called an anion-active, *e.g.*, $RSO_3Na \rightleftarrows (RSO_3)^- + Na^+$. Chlorides of high molecular weight quaternary ammonium bases are examples of cationic active agents, *e.g.*, $R(CH_3)_2\ (C_6H_5CH_2)NCl \rightleftarrows R(CH_3)_2\ (C_6H_5CH_2)N^+ + Cl^-$. The choice of the proper type of surface active agent is influenced by the other ions which may be present in the system under consideration.

The surface active agents are according to their specific performance tests better characterised as wetting, foaming, dispersing, emulsifying, and detergent agents.

Surface active agents can be broadly classified into the following categories anionic, nonionic, cationic and ampholytic.

Application of surface active agents in the leather processing

The properties of surface active agents will depend on the length of the carbon chain, balance, active groupings involved and on these, will depend the ultimate use to which these products could be put to, *i.e.*, for wetting, penetration, detergency or emulsification etc.

Surface active agents are used in almost every operation of the leather processing.

1. *Soaking agents :* Soaking of green or wet salted hides and skins of course presents no problem to the tanners but when dry salted or flint dried hides and skins are used for processing and specially in cases where hides and skins are coming of fallen stock and they have not been cured properly before drying, the soaking operation has to be speeded up if better leathers are to be prepared ; usually small amounts of sodium hydroxide, sodium sulphide, sodium tetrasulphide or salts of polyvalent ions like citrate, phosphate etc. are commonly used. But sometimes these agents are not enough and additional surface active agents have to be used. Dehydol, Mollescol BM., Pencrolin L, Teepol etc., are the different products marketed by different manufacturers. Some of these are only wetting agents while others are mixed blends of wetting agents and a preservative ; Mollescal BM. is supposed to be composed of—

Monoethanolamine or Butanolamine ...	57.5%
Neckal (Isobutyl naphthalene sulfonic acid) ...	11.5%
Trichlorophenol	6.5%
Water	2.5%

The surface active materials used mostly in soaking belong to the nonionic and anionic category. These materials mostly belong to the following types :

(*a*) fatty alkyl sulphates

(*b*) alkyl aryl sulphonates

(*c*) polyethylene oxide based nonionics.

It is to be noted that these materials are used only in limited quantities for if used in excess they remain absorbed on the pelt and get precipitated in the liming process; though they do not show any detrimental effect in the course of tanning and subsequent operations, they affect the final glaze of the finished leather. However, in case of hides and skins, intended for such types of leathers as are not to be used for pigment or aniline finishing and require only dull finish this excess will not affect.

2. *Degreasing of hides and skins :* Degreasing of sheep skins specially those going to be used for suedes etc., is one of the special processing steps. In India, of course, because the animals, are ill-fed and undernourished, this problem does not arise so often, but is common in case of skins from some of the hilly regions and some other parts. This natural grease and fat in the

pelt causes a constant source of trouble in soaking and liming and later operations. (The surface active agents indicated in the soaking operations generally serve the purpose.) The main purpose of these agents in this process is to emulsify and remove the natural greases, and allow the proper soaking of the hides and skins for subsequent operations.

3. *Liming operations—Penetrating agents for depilants :* The quality of a finished leather mostly depends on the pretanning operations and liming is one of the essential steps in this stage. The proper use of a penetrating agent with depilants not only speeds up the liming operation, but also regulates the action uniformly throughout the thickness, regulating the swelling, opening up of the fibres and removal of soluble proteins, speeding up the liming action and resulting in finer grain. The material most commonly used for this purpose is dimethyl amine sulphate. One additional advantage in using this chemical is the production of fine grain.

4. *Bating operation :* Bating is another essential item specially for very fine leathers like glazed kids, box and willows, velvet leathers etc. Surface active materials generally of the type of (*a*) sulphated fatty esters and (*b*) sulfated fatty alcohols are sometimes used. It is a regular practice to either incorporate these materials in the ready mixed bating and deliming agents or to use them during the bating operation. This incorporation gives not only a more uniform and efficient bating operation but also shortens the time of bating.

5. *Tanning operation :* In the two major types of tanning that is vegetable tanning and mineral tanning, the surfactants have their special role to play.

In vegetable tanning, the action of tannins is speeded up by the use of anionic surface acting materials like alkyl aryl sulfonates. These alkyl aryl sulfonates if properly formulated sometimes show a tanning effect by themselves. These are the constituents of the syntans which as every tanner knows play such an important role in tanning. They effect speedier penetration of the tannins, affect the particle size of the tannins, give a uniform action of the tannins on pelts and give better yields. The biggest role of the surfactants in this field is to improve wettability and thereby make available to the tanner a tool for overcoming the permanent hardness. Besides the anionics, sometimes nonionics can also be used in vegetable tanning. The incorporation of the surface active agents has to be done judiciously, since these surfactants affect the charge conditions of the leather and subsequent modifications are required if the leathers are to be finished in fancy light coloured shades.

In chrome tanning also the surface active agents are now used on an ever increasing scale. It is a common knowledge that chrome tanned leathers if allowed to dry cannot be soaked back. In such cases if a small amount of any nonionic or cationic wetting agents is applied before the leathers are dried, the agents enter the chromium complex, displacing the aquo groups which are displaced in the course of drying. Such leathers are readily wetted back after drying. Due to this property, the use of wetting agents forms an essential use in the production of suedes, etc., where the leathers are to be dyed after drying. The cationic surfactants can also be used to regulate the uptake of chromium from a liquor which is not correctly made and contains a larger amount of anionic constituents. In addition to this, the surfactants speed up the penetration of chrome in tanning operation and thus speed up the tanning.

Another important use to which these surfactants have been used recently as reported by workers in America is that of tanning and fatliquoring in a single bath using these surfactants as stabilizers. In such a case, the chrome liquors which in themselves contain generally all the three types of ionic constituents, *i.e.*, anionic, nonionic and cationic, are further stabilized by nonionic agents and the anionic fatliquor incorporated ; to balance the overall charge a cationic surfactant is also introduced. The use of such a mixture stabilized by the necessary surfactants can be used to give a satisfactory tanning and fatliquoring effect in the same bath.

Other uses of surfactants in mineral tannage are regulating the action of chrome in mixed tannages like semi-chrome, semi-alum or chrome retan operations where these materials could be used judiciously to condition the leathers for subsequent operations of dyeing and fatliquoring, by adjusting the charge conditions of leathers which play so important a role in these operations.

Besides the vegetable and mineral tannages, surface active agents also find use in oil tannage to make the oils more wettable and better absorbed by the wet pelt ; otherwise the skins have to be drummed for a longer time. The use of nonionic wetting agents is preferred. After oxidation and completion of oil tannage, excess of free oils is to be removedand in this operation again surface active materials having mostly emulsifying properties find use. In this operation, these could be used alone or in combination with other alkalies which convert the oil into soaps and thus remove the free oils.

Another field of application of these surfactants is in the field of syntan tannages. It is a common knowledge that syntan tannages unlike vegetable tannages are mostly due to the linkage of NH_2 groups of collagen with the reactive groups of syntans and as such their further properties of taking up fatliquor and dyes are impaired. This is of utmost importance in view of the ever increasing use of syntans for tannages, specially in white tanned leathers where the property of the leathers for correctly absorbing the fatliquors is to be corrected by the use of suitable surface active materials.

6. *Oiling, fatliquoring and stuffing :* By far the largest use of surface active agents of all types is in this operation. The various types of materials used are as follows :

(*a*) Soaps
(*b*) Sulfated fatty acids/oils
(*c*) alkyl aromatic sulfonate
(*d*) fatty alcohol sulfate
(*e*) Sulfated polyethylene ethers.
(*f*) phosphated oils
(*g*) Igepons *e.g.*, fatty acid amide compositions
(*h*) Quaternary ammonium compounds, etc.

A judicious blend of these materials with oils, fats, and waxes is done by the trade for specific application for particular types of leathers. Most of the commercial fatliquors imported from the foreign countries contain a blend of the various types of surface active agents to give the desired effect to the leather. The main function of these materials besides emulsification is the lowering of the interfacial surface tension and absorption of the materials either from water emulsions as in fatliquoring or oily emulsions as in stuffing. Further details of this aspect are dealt with in another paper.

7. *Dyeing :* The surface active agent plays an important role in dyeing and there are various proprietory products now available to the trade. The

main function is penetration and level dyeing. The main types of materials used for this purpose are :

(*a*) Sulfates and sulfonates of high surface activity.

(*b*) Quaternary ammonium or phosphonium salts as dyeing assistants.

(*c*) Nonionic material specially in stain dyeing of leathers with penetrating effect.

Levelness and richness of the shades are important criteria in dyeing of leathers ; specially in lighter shades they are of utmost importance. While no doubt the basic qualities of dyes play an important role, additives like surfactants have to be used to get the right effect.

8. *Finishing :* Finishing though the last operation of leather processing is one of the most important operations and like the pretanning operations can make or mar the leathers. In this operation, the surface active agents have to play different roles.

(*a*) Clearing the leather surface of oiliness before finishing :—This is an important factor when leathers are to be glaze finished. Usually a dilute solution of ammonia is used but detergent is also sometimes used with better effects as this does this more uniformly and efficiently. In the case of leathers where paste drying is employed, the surface has a coating of the adhesive used in pasting. Usually such leathers are given a scrubbing with brush on the surface with hot water containing a little amount of surface active agents.

(*b*) Formulation of the binders for leather finishing : Synthetic resins in water emulsion forms are being used on an ever increasing scale in the finishing of leather. A variety of anionic, nonionic and cationic surfactants are used in the course of emulsion polymerisation keeping the polymerised materials in emulsion state. Some of the different types of synthetic resin emulsions used in the leather finishing are acrylonitrile, acrylic ester copolymer, polystyrene, styrene-butadiene, butadiene-acrylonitrile, vinyl chlorides—vinylidene, neoprene, acrylics, polyvinylacetate etc.

(*c*) Preparation of finishing auxiliaries for leather finish formulation : In the formulation of the finishes, various other materials are used in which surfactants are required essentially.

(i) Preparation of water based pigments and colours : In bringing the various materials used in pigment finishes to a homogeneous phase, the surface active agent plays an important role and it has a dual role *i.e.*, to emulsify the various ingredients and acting as plasticiser for the natural and synthetic binders and vehicle used in the manufacture. The sulfated oils and sulfated alcohols etc., are the main types used for the purpose.

(ii) In a number of finishes, waxes and other specific materials like plasticisers etc., have to be incorporated in the formulation and again surface active agents have to be used for dispersing them in water. Normally, anionics are preferred as the general finish is anionic by nature

(iii) Preparation of lacquer emulsions for leather finishing—is one of the essential fields using the surfactants. While no doubt the lacquer emulsions by themselves give a better finish the quality of the finish is decreased in respect of inertness to water ; but the low cost and better qualities compared to a. water based finish enhance their value. In order to have better type lacquer finishes, use of pigments ground in the nitrocellulose or other synthetic resins and other gloss giving materials like alkyds is preferred and as such in this field also surface active agents having emulsifying action in keeping with the proper charge conditions are used extensively.

Other uses : (*a*) In addition to the various specific uses of the surface active materials indicated above these materials also find use in a variety of other subsequent operations of leather fabrications. Some of them are enumerated :

formulations of stains, adhesives, polishes, creams, top dressings for leather goods etc., rejuvenating or reinvigorating of used leather goods for reuse.

In all these operations surface active agents having specific actions like emulsifying action, wetting action, detergency, germicidal effects are used depending on the purpose where they are used.

(*b*) Another important use is in the scouring of wool and hair the bye-products of leather.

Hair and wool are the essential tannery bye-products. But before they could be used in the preparation of various materials these must be degreased. The wool grease is one of the essential materials used in the stuffing grease of leather. Although organic solvents were once used extensively, due to high cost, the use of surfactants for this purpose of degreasing is becoming very common as this makes the process very economical. Besides it does not affect the physical properties of the wool. It may be mentioned that wool grease besides finding use in leather stuffing is extensively used in the preparation of the material known as lanolin used in cosmetic preparations.

(*c*) The last item that may be mentioned here is in the utilization of leather wastes. The various leather wastes like cuttings, trimmings etc. generally used either for the preparation of leather boards used extensively in the shoe and leather goods trade or cushioning materials for packing have to use these surface active materials for conditioning before using them for these purposes.

It is thus evident that although the amount of the surface active materials that may be used in the processing of leather or fabrication of leather goods may not be as substantial as the amount of other materials like tanning materials etc., the role they have to play is no less important than any other essential materials used in leather processing.

EMULSIFIERS FOR USE IN LEATHER INDUSTRY—PART I

BY

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ABSTRACT

The different classes of emulsifiers have been outlined with details of their preparation and uses in leather manufacture. The mechanism of emulsification is briefly described. Certain emulsifiers of the anionic, cationic and non-anionic types were prepared at this Institute in a laboratory scale, and utilised for the fatliquoring of leather in small lots. Interesting results have been obtained and it has been proposed to continue these investigations in order to develop the processes on commercial scale after examining the economics of the processes.

The spontaneous formation of an emulsion when any two liquids are mixed is only an exceptional behaviour since thermodynamically this system is unstable. In order to get a good emulsion of optimum stability, the presence of a third substance—an emulsifier—is generally necessary. The emulsions that are of particular interest to the tanner are the oil in water type, *i.e.*, where water is the dispersing medium ; the work undertaken concerns with this aspect only. Very recently, however, it has been reported water in oil type emulsions could also be used for fatliquoring leathers.

Emulsification phenomenon is a part of surface activity which also includes other effects such as wetting, detergency, foaming etc. By far the most important usage of surfactants is for emulsification of oils, since such emulsions are needed very much for the fatliquoring operation. While the fatliquor and the fatliquoring operation are dealt with in another communication dealing with sulphated oils, the present paper is concerned with certain other types of emulsifiers.

Briefly, emulsifiers are classified as anionic, cationic, non-ionic, ampholytic etc., depending upon the charge associated with the hydrophilic group. Soaps and sulfated alcohols are examples of anionic type while, quaternary ammonium salts of higher fatty acids belong to the cationics.

The industrial importance of soaps as emulsifiers has decreased to a great extent, owing to their instability towards hard waters and acidic media, where sulphated oils and other synthetic emulsifiers of allied type have been found to be better suited. Further, between sulphated oils and other emulsifiers, the latter are preferred as only smaller amounts (less than 10%) of them would give satisfactory results. Moreover, emulsifiers could be tailored more easily to the specific needs of the industry, particularly for the fatliquoring of different classes and varieties of leathers. A third important factor for consideration is that an emulsion should be stable for the required period only but breaking at a subsequent desired stage. In fatliquoring leathers, the fatliquor should be stable, in contact with the leather, but should break so that the fat be deposited inside the leather to impart desired properties. Depending on the type of leather required, the depth to which the emulsion penetrates, and when it should break, are of significance. This is exemplified in shoe uppers which should not be too soft but also not too bony which is achieved by a little penetration of oil and not too much, whereas exactly opposite is the case with gloving leather where full penetration and breaking up emulsion within is necessary. Moreover, with chrome tanned leather which is positively charged anionic emulsions fix and cationics penetrate while, opposite is the case in vegetable tanned leather.

An emulsifier molecule has a hydrophilic and a hydrophobic part. The more important raw materials for the typical hydrophobic group are the natural fatty oils, acids, alcohols, olefins like propene, butene, petroleum hydrocarbons etc.

In this Institute, fatty oils and mineral oils of kerosene type were chosen since these are available in plenty and cheaply.

Anionics : Fatty acids were made from Pongam, fish, neatsfoot, linseed, coconut and castor oils by adopting the soap formation and acid hydrolysis of the soap process, since equipment for other processes are not at present available in this Institute. Though the process adopted is not economical, later on fatty acids obtained from other sources could be used for the subsequent reactions.

The fatty acids were sulfated to see if these are better than the corresponding sulphated oils. Monoglycerides were prepared by reacting the fatty acids with glycerol for a long time (more than 10 hours) and sulphating them. Monoethanolamide and amides, were prepared by reacting the fatty acids with monoethanolamine and ammonia respectively. These two were also sulphated. The different fatty amides themselves were good emulsifiers. Thus twenty four products were made.

Cationics : (1) Coconut fatty acid and triethanolamine were taken in molecular proportion and refluxed for six hours.

(2) Amide was prepared from Immergan sulfonate and reacted with formaldehyde and pyridine in presence of HCl as catalyst.

(3) Oleylamide was also reacted in the same manner.

(4) Coconut fatty acid and diethanolamine were reacted in molecular proportions at a high temperature.

Nonionics : The fatty acids referred to under anionics were reacted with polyethylene glycols of molecular weight 400 and 600 at high temperature (120–150 °C).

The monoglycerides themselves were moderately active nonionic emulsifiers.

Different amounts of these emulsifiers were used to emulsify neatsfoot oil and the resulting emulsions were used to fatliquor small pieces of chrome and vegetable tanned leather. Among the products prepared, coconut monoglyceride and castor monoglyceride sulphates, sulphated monoethanolamide, pongam amide, Linseed acid polyethylene glycol condensate, neatsfoot oil amide, its polyethylene-glycol condensate, fish oil amide and its poly ethyleneglycol condensate gave satisfactory fatliquoring effects in small cut pieces. Some of the products are comparable with imported ones and large scale experiments using them in the tannery are just now undertaken and if successful, the products will be prepared on pilot plant scale to ascertain the economics of the production in order to commercialise the processes.

Other uses of emulsifiers in preparing pigment finishes, binders, etc., are there and detailed investigation of the problems involved will be undertaken shortly.

It may be mentioned that in Germany during the war years, chlorinated and sulpho-chlorinated products like Immergan, Derminol oil, Derminol fatliquor etc., were manufactured in a large scale to replace fatty oils that had become scarce at that time in that country.

Work of similar nature using kerosene and diesel oils following the Reed reaction was also attempted at this Institute, in order to use them for fatliquoring instead of the costly fatty oils.

The limitations to work of this nature—manufacture of emulsifiers—are the utterly inadequate availability of the more important raw materials like polyethylene glycols, ethylene oxides, nitrogen based carbon compounds like pyridine, quinoline etc., as also the equipment needed for such reactions in our country.

However, it is hoped the work that has been initiated in this field and which has been giving encouraging results till now would ultimately lead to the manufacture of atleast a few useful emulsifiers belonging to the different classes.

SULPHATED OILS PREPARED AT CENTRAL LEATHER RESEARCH INSTITUTE AND THEIR USE ON LEATHERS

BY

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ABSTRACT

The use of sulphated oils and the importance of the fatliquoring operation in leather manufacture have been described. The different classes of emulsifiers are enumerated specially to bring out the important role of sulphated oils in leather industry. Processes that have been developed at the Institute for sulphation of various oils like Pongam, Fish, Neatsfoot, Ricebran and Tobacco seed are dealt with at length, along with the application of these oils on different varieties of leathers.

It is well known that unfatliquored chrome tanned leather when allowed to dry becomes "bony" and hard. This is generally attributed to the cross linking of the adjacent fibres thereby preventing their free movement. Thus there is the imperative need for the incorporation of lubricants, which process is conveniently known as fat-liquoring and stuffing. During these operations the wet leather fibres are coated with an oil film which prevents their adhesion during drying. The amount and the nature of the oily materials used and their distribution in the leather layerwise determine the characteristics such as tensile strength, fullness, softness etc.

Fat-liquors are blends of emulsifying agents and neutral oil (vegetable, marine and mineral). The emulsifying agent stabilizes the emulsion of oil in water and serves to carry the oils into the interior of the skins, where it is deposited by subsequent breaking of the emulsion due to the neutralisation of the charges.

Natural products such as lecithin, egg-yolk etc., are good emulsifying agents. The emulsifier mainly constitutes a hydrophobic group (water repelling) and hydrophilic (polar) group having a positive or negative charge. Emulsifiers could be cationic, nonionic, anionic or ampholytic. Though soap is the earliest known anionic emulsifier, its use is a bit limited as it is unstable to hard water and acids. The materials that are used in the preparation of fat-liquors are the sulphated and sulphonated products of vegetable, marine and mineral oils. The most common of these are the sulphated oils of vegetable and marine origin. The sulphated products are anionic emulsifiers.

In general the agents used for the sulphation are concentrated sulphuric acid, oleum, chlorosulphonic acid etc., and combination of these with acetic anhydride. By varying the conditions of reaction a variety of products may be obtained. Very briefly the process of sulphation on large scale may be described as follows :

Sulphuric acid is sprayed slowly into an oil under conditions of vigorous cooling and stirring. This process may take 2–3 hours or even more depending on the percentage of sulphuric acid and the temperature of sulphation. When the reaction is complete, cool brine is added and agitated. The excess sulphuric acid is washed out into the brine and the ester floats on top after settling. The acid water is run off and the sulphuric acid ester is neutralised with ammonia, caustic soda or other alkalis and adjusted to the desired pH value.

Brief description of the processes for the manufacture of sulphated oils from indigenous oils such as Pongam, Fish, Rice bran etc., which are developed at C.L.R.I. are given below. Though the processes for the manufacture of sulphated oils from fish, rice bran etc., have already been developed at the laboratory level previously, it has been found necessary to modify the processes to get still better products having better emulsifying properties and giving emulsions of greater stability.

1. *Sulphated pongam oil :* The process has already been standardised in the laboratory as well as at the Pilot Plant and it has reached the stage for the commercial exploitation.

2. *Sulphated fish oil :* Concentrated sulphuric acid (about 25% on the weight of the oil) is added slowly to the raw oil at moderately high temperature and it is given the usual brine wash. Then it is allowed to settle till two clear layers separate. The lower acid layer is drawn off and the sulphuric acid ester is neutralised with caustic soda solution (of about 25% strength) to the optimum pH value. The product gives stable emulsions with fairly good emulsifying properties with water and the nature of the emulsion also varies from white cream to translucent depending on the characteristics of the fish oil used.

3. *Sulphated neatsfoot oil :* Concentrated sulphuric acid (about 25–30%) on the weight of the oil) is slowly sprayed into the raw oil at a very low temperature and then washed with the brine solution (15% strength). Then, it is allowed to settle for 3–4 hours, when two clear layers separate. The lower acid layer is removed and the ester is neutralised to a pH value of 5.8–6.5 with 25% solution of caustic soda.

4. *Sulphated rice bran oil :* The oil is treated with 30% concentrated sulphuric acid at a very low temperature and then washed with 15–20% solution of common salt and allowed to settle till two layers separate. The lower acid layer is drawn off and the ester is neutralised to the optimum pH value with 20–25% solution of either caustic soda or caustic potash.

5. *Sulphated tobacco seed oil :* The raw oil is treated at a very low temperature with concentrated sulphuric acid (20–25% on the weight of the oil) and then washed with a saturated solution of sodium chloride after giving sufficient time for them to react. Then it is allowed to settle for overnight when two layers separate out. The lower acid layer is removed and the ester is neutralised with caustic soda solution.

Application of sulphated oils on leathers : Fat-liquors are obtained from the above sulphated oils by blending each of them in suitable proportion with neutral (vegetable or marine) oil and mineral oil ; these are tried on leathers along with controls, *i.e.*, the commercial fat-liquors such as Cremol F. It has been observed that the effects such as fullness, softness, roundness etc., produced by the fatliquors prepared in this Institute are at least equal if not superior to those produced by Cremols in different types of leathers such as Box and Willow Side, Upholstery, Glazed Kids etc. Sulphated Pongam oil can be safely used in place of Cremol F for Box and Willow sides. Similarly sulphated fish oil is being used in the manufacture of upholstery leather from bark tannage and combination tannages, gloves and garment leathers. The sulphated products from fish and neatsfoot oils are found quite satisfactory, giving encouraging results when tried on glazed kids. Sulphated tobacco seed oil and sulphated rice bran oil are under investigation for their suitability for other types of leathers such as suedes, semichrome etc.

Further, it may be mentioned here that the use of mineral oil and its effect on fatliquoring of leathers will be investigated in order to see whether the cost of fatliquor could be reduced still further as the price of mineral oil is very much lower than fixed oils. The different sulphated oils will be separated into various fractions like sulphated groups, neutral oil, free fatty acids, hydroxy acids etc., following well-known analytical methods and the role each one of these constituents plays in the fatliquoring operation will be studied.

Discussion

Mr. J. Ghosh, (Small Industries Service Institute, Madras) : In using sulphated or sulphonated oil, a part is wasted for emulsification. Could not a suitable surface active agent be used ?

Dr. D. Ramaswamy (C.L.R.I., on behalf of the author) : Use of 0.1% surface active agent is employed in fatliquoring ; but the medium used is a sulphate water mixture and not pure aqueous.

CATIONIC, NONIONIC AND MULTICHARGED FATLIQUORS

BY

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ABSTRACT

The developments in the field of fatliquoring, using anionic, cationic and anionic products, singly or in blends or in stages, are outlined and the scope for future investigation and development is indicated.

THE UNIT PROCESS OF SULPHONATION

BY

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ABSTRACT

Manufacture of a good number of leather auxiliaries involves sulphonation (or sulphation) as an important step. The essentials of this process, *i.e.*, its chemistry, plant procedures and equipment are presented.

Introduction

The object of this paper is to present the essentials of the unit process of sulfonation to those who are interested in the manufacture of leather auxiliaries like the synthetic detergents or the surface active agents. A good many of these involve sulfonation (or sulfation) as one of the important steps in their manufacture. An understanding of the essentials of sulfonation as a unit process would be of immense value in simplifying the efforts that may be made by individuals for locally manufacturing auxiliaries of this type.

Sulphonated tanning auxiliaries

The synthetic tannins, or ' syntans ' are substitutes for the naturally available tanning agents and are, in general, made by sulfonation of phenol, cresol or naphthalene, etc., and the subsequent condensation of the sulfonated aromatic with formaldehyde. These products are water soluble, and exhibit marked tanning action. They are ordinarily used in conjunction with other tanning agents such as chrome, vegetable or alum. Sulfonation, one of the stages in the preparation of syntans, is important in that it confers solubility in water, on the product.

The surface active agents used in leather industry comprise, apart from soap itself, a good number of synthetic detergents, a majority of which are obtained by sulfation or sulfonation of alkyl and aryl compounds and also of natural fats and oils. They are used in removing fat (or degreasing), in tanning and dyeing, and in fat liquoring (*i.e.*, putting the fat back into the hide to restore it to its natural, pliable state). In degreasing, the surface active agent acts as an emulsifier, bringing about intimate contact between the grease and solvent in the presence of water. In tanning, the surface active agent acts as a dispersant for the vegetable tan, and also as a penetrant or levelling agent, to ensure thorough and uniform coverage. In fat liquoring, it acts as an emulsifier to carry the oil into the pores of the wet leather, and deposit it. The surface active agents are also used in other subsidiary operations such as dehairing, cleaning of raw hides, deliming, soaking of dried skins, and hydrolysis operations in glue manufacturing. Here also it is the sulfonic acid group which confers on the compound these highly desired properties of wetting and emulsifying.

Sulfation and sulfonation

The processes of sulfation and sulfonation do not differ greatly, both involving, as they do, reaction of a raw material with strong sulfuric acid under similar operating conditions. The distinction between the two is that, while in a sulfated product the linkage is carbon to oxygen to sulfur, in a true sulfonate, the sulfur is directly linked to the carbon. The chemistry of the process is sufficiently well-known.

Sulfonating agents

Among the chemicals used for sulfonating, sulfuric acid is the most common.

$$RH + H_2OSO_3 = RSO_2OH + H_2O.$$

Water being a by-product, the rate of sulfonation gets decelerated as the reaction proceeds. There is a limiting SO_3 concentration (designated as π by Guyot) at which the sulfonation reaction stops. This value of π depends upon the compound undergoing treatment and is independent of temperature, agitation or catalysts. Considerable acid is thus obviously wasted by ordinary methods of sulfonation, by reaction with the alkali during neutralization that is carried out towards the end. Some of the procedures that are adopted, where possible, for reducing the excess acid required, are (1) use of reduced pressures, (2) addition of SO_3, (3) azeotropic distillation of water, or (4) use of dehydrating agents like acetic anhydride, phosphorous pentoxide and boron trifluoride. It is also usual to provide sulfonators with devices for heating to enable continuing the reaction during the final stages which would otherwise be slow because of the decelerating influence of water.

The decelerating influence of water can also be obviated by the use of oleum (100% sulphuric acid containing dissolved SO_3) in preference to sulfuric acid. By a judicial combination of oleum with the spent acid for the sulfonation, and modified procedures, only a small excess of SO_3 can be made to be present at any stage of the reaction, thus inhibiting the tendency to over-sulfonation and also effecting economy in the amount of SO_3 that must be employed. Oleum is also invariably used instead of sulfuric acid in cases where the reaction proceeds with difficulty even with the application of heat.

Sulfur trioxide can be used for sulfonation of practically all classes of organic compounds. Unlike reaction with sulfuric acid, no water is formed in this case.

$$RH + SO_3 = RSO_3H$$
$$ROH + SO_3 = ROSO_2OH$$

Its action is so vigorous that it has a tendency to carbonize the organic compound when applied directly. The technical use of sulfur trioxide usually involves, (1) low temperatures, (2) use of solvents like sulfur dioxide, carbon tetrachloride, tetrachloroethane, (3) presence of ordinary sulfuric acid, (4) application as a vapour and (5) use as an adduct, *e.g.*, N-pyridinium sulfonic acid, dioxane sulfotrioxide, and thioxane sulfotrioxide. One special advantage of using sulfur trioxide in the production of synthetic detergents such as lauryl sulfate or alkyl aryl sulfonates is that it gives a product of 90 to 100% active ingredient and may be compounded with phosphates or builders other than sodium sulfate. The production capacity per unit installation is also greater, since only a slight excess over the theoretical amount of SO_3 is required. As against this the use of oleum or concentrated sulfuric acid would result in the presence of a considerable amount of sodium sulfate from the excess sulfuric acid, or would give rise to a spent-acid disposal problem. The use of sulfur trioxide, however, has the disadvantage of the greater difficulty in handling the reagent, greater heat of reaction, and frequent need of solvents to obtain light-coloured products.

The other reagents used for sulfonation are sulfuryl chloride (SO_2Cl_2), sulfites and bisulfites, chlorosulfonic acid (O_2SOHCl) and miscellaneous agents like acid sulfates, hyposulfites, etc.

Excellent reviews on sulfonation have been made by Lisk[1] and Gilbert and Jones[2] under the Unit Process review in the Journal, Industrial and Engineering Chemistry.

Plant procedures

Process conditions for sulfonation have developed over the years mostly on empirical basis.

A basic process for the sulfonation of a simple aromatic, such as benzene, consists of adding 1½ to 2 moles of 98–100% sulfuric acid to 1 mole of benzene, refluxing the mixture, and finally heating to 150–200°F. to complete the reaction. The total batch time on a commercial scale may be 3 to 8 hours. As the reaction proceeds, the water formed dilutes the sulfuric acid and when the acid strength goes below 75–80%, the reaction proceeds slowly. This creates the need for use of excess acid. Several improvements have been made in this process. For example, in the Tyrer process benzene vapour is introduced into 90% sulfuric acid maintained at about 200°F. Unreacted benzene vapour and water vapour are removed from the top of the vessel, condensed and the benzene phase recycled. For high boiling aromatic compounds, air or inert gas or an additional volatile solvent such as low boiling hydrocarbons may be added to obtain the partial pressure effect. It can, however, be seen that much depends on the nature of the raw material, for rendering feasible the application of such procedures.

However, for detergent use, quality considerations for the final product limit the combination of conditions that can be employed. In the manufacture of detergents it is usually preferable to sulfonate substantially to completion so that no additional processing is required to remove unreacted aromatics from the detergent product. The effort of the detergent producer is to formulate conditions which would yield a product of light colour and minimum odour, which can be usually achieved with mild sulfonation. Hence, in a typical process, oleum is used and a lower temperature is adopted even though it entails the use of increased amount of acid (about a third extra) which, however, helps to reduce the residual oil after sulfonation considerably. 85°F is the temperature frequently preferred, and a product of light colour and better quality is obtained. Reduction of temperature to the still lower limit of 50°–60°F may be beneficial in improving the colour of the product still further, but it is not used commercially since it entails the use of refrigerated water which may require revision in plant equipment. At the end of the sulfonation, the excess acid is neutralised and the product is marketed as sodium-sulfate—sodium sulfonate mixture.

But recent requirements demanded addition of considerable amounts of phosphate builders to the detergent formulations, and this necessitated the reduction of the large sulfate content in the final product. The acid mix after sulfonation is diluted with water, and a lower phase of sulfuric acid of about 80% concentration is settled out at temperature 120°–140°F for three to eight hours. As sulfonic acid is substantially insoluble in 80% sulfuric acid, the losses of sulfonic acid by this method are small. The lower sulfuric acid phase is withdrawn, and the upper phase containing the sulfonic acid is neutralized to yield a product of sulfate content sufficiently low to permit easy use of the product in phosphate formulations. The spent sulfuric acid, however, cannot be used again directly for detergent sulfonation, but may be reprocessed or sold for other purposes.

It is also preferable, in acid settling procedures, to limit the time and temperature as much as possible to minimize the formation of undesirable materials which increase the colour of the neutralised product. But the quick removal of the excess acid produces a more uniform product, of a lighter colour, and hence a higher temperature (120°–140°F) may be used during settling to reduce the viscosity of the upper phase for minimizing the time required. With this end in view, solvents have been tried, instead of heating, and have been found effective but for the great disadvantage that they involve the additional process of evaporating ultimately. Extraction processes involving use of concentrated hydrochloric acid as a wash to remove sulfuric acid, the residual HCl in the upper layer being removed by air blowing, have also been proposed. While centrifuging definitely helps in quickening acid settling, it has not yet been practised commercially, high corrosion rates in the centrifuge having been encountered in the test work.

Thus the nature of the product that is ultimately obtained depends much on the washing procedure. This is particularly so in the case of products prepared from fats and oils. Throughout the washing procedure all the conditions must remain constant if uniformity of product is desired. Temperature control is almost as important during washing as in the actual sulfonation. The amount of wash water, the length of time required for complete removal of wash water, the type of agitation, the size and shape of the wash tank, all have a bearing on the final product. Agitation by air may have a tendency to emulsification which would interfere with the subsequent separation. If it is necessary to transfer the mass to a separate finishing tank, this should be done after the acid wash is removed.

The tendency for emulsification during agitation while washing, in the case of certain materials like oleic acid under sulfonation, is greater, particularly if one tries to neutralise the excess acid entirely. In such cases the wash is preferably left on the acid side to get a complete separation.

Washing entails, however, certain inevitable loss of material. The wash water carries away some sulfonic acid and salts from the neutralization of excess acid, apart from glycerine in the case of glycerides. The loss may be of the order of at least 4% based on the original oil in the case of glycerides, the value depending much on the efficiency of operation.

The time for sulfation depends much on the viscosity of the raw material used. Thus oleic acid and butyl oleate sulfate almost at the same rate, both having low viscosities.

Special problems arise in the case of sulfation of cod oil and tallow. In the case of cod oil, because of its unsaturation the reaction must be rigidly controlled, and the oil is precooled before starting the reaction so as to introduce as much acid as possible before the large increase in viscosity takes place and consequent very poor agitation and heat transfer. On account of the heat of neutralization it is often times desirable to give the mixture a quick water wash and then neutralize the remaining excess acid with careful attention to temperature control. In the case of tallow, it has to be melted and run. In this instance, therefore, cooling is difficult as the tallow tends to congeal on the coils. There are compensations, however, as some types of products require no washing, in which case the entire mass is diluted with water and partially saponified to form a sulfated glyceride soap.

Equipment

Both batch and continuous operations are in vogue depending upon the nature of the raw material used. The batch operations are more common. Stone crocks upto 5 gallons capacity were used in the early days. Cast iron apparatus are suitable for sulfonations with concentrated sulfuric acid of 88—98% strength. For oleum or for mixtures containing free SO_3 it is advisable to employ steel equipment. For higher capacities, generally, lead-lined talks with vertical agitator with side arms operating at slow speeds are used. The vessels can also be of monel or nickel clad steel, and preferably provided with a jacket and coils which can be used for cooling purposes or alternately for heating when so required. Enamelled or glass lined vessels can also be used. If the mass is very viscous, the agitator may be made of the turbine type. The coolant through the jacket and coils is usually city water but where necessary, refrigerated water may be circulated. In some cases liquid carbondioxide has been tried by direct introduction into the reaction to obtain much lower temperature, but if the reaction product has a very high viscosity, the gas cannot readily escape and foaming occurs to a considerable extent.

Figure 1, illustrates a typical industrial batch sulfonator. The figure is self-explanatory.

Where sulfonation gives rise to solid, doughy, or viscous masses that are not stirrable in conventional batch sulfonators, Ball Mill type of sulfonators may be used, as in vogue in the manufacture of naphthionic acid from

1-naphthylamine, sulfanilic acid from aniline, and 2-naphthol-6-sulfonic acid from 2-naphthol.

Continuous methods of sulfonation can be carried out where (*a*) the organic compound (like benzene or naphthalene) can be volatilized, (*b*) where the reaction rates are high as in chlorosulfonation of paraffins or sulfation of alcohols and (*c*) where the production is large as in the manufacture of detergents such as alkylaryl sulfonates. But the capital expenditure and process development costs are higher thus limiting liberal adoption.

As has already been stated earlier, for volatile organic compounds such as benzene, the water of reaction can be removed as an azeotrope with benzene, and Guyot applied this principle for the sulfonation of benzene by using an excess of benzene in the conventional equipment. Guyot's batch process has since been converted into an efficient continuous process, by which the capacity has been increased nearly ten times.

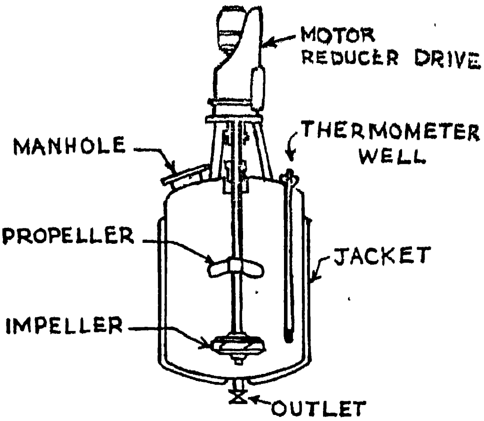

FIG.1. BATCH SULFONATOR

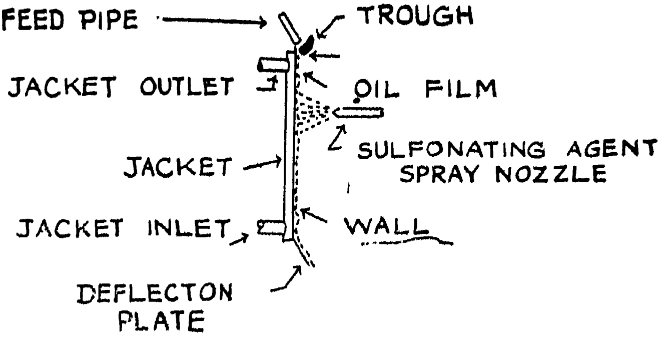

FIG. 2. CONTINUOUS SULFONATOR

The sulfonation of saturated and unsaturated fats and fatty oils and the sulfation of fatty alcohols can be carried out in the continuous apparatus shown in Figure 2. The fatty compound is delivered through a charging pipe on to a trough disposed at the top of a jacketed wall, and discharges therefrom through a slit as a thin film of liquid which flows down the exposed surface of the wall. At the same time, a sulfonating agent is sprayed through a nozzle into the descending film of liquid. The sulfonic acid produced passes downward and is guided to a deflector plate at the lower edge of the wall. The reactants thus get mixed under conditions that permit excellent temperature control without the necessity of using a considerable excess of sulfonating agent.

Another continuous sulfonation equipment which would be of interest is the one developed in the production of sulfonated monoglycerides wherein the materials are introduced at the top of a tower and flow down over a series of cooling coils and paddles with continuous discharge from the bottom. This is illustrated in Figure 3.

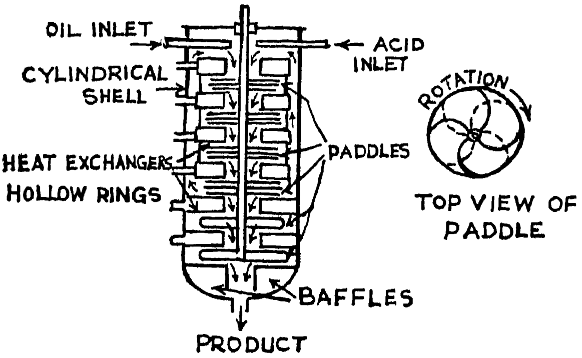

FIG. 3. CONTINUOS SULFONATOR

Several novel designs of the reactor have been suggested to improve sulfonation. A continuous process involves the use of a vertical tube reactor fitted with internal cooling coils kept filled with acid, and the oil, pumped from the bottom of the tower rising through the denser acid phase, being withdrawn as partially sulfated oil. In another system which is similar in principle to the one shown in Figure 2, the sulfating agent and the fatty alcohol are introduced into a vessel in opposing spray patterns, the sulfate that is formed falling on to the bottom of the vessel, and cooling being provided by a stream of air admitted at the top through a spray trap. The advantages of this procedure are the short reaction time and the intimate contact achieved with the acid, alcohol and cooling medium.

Conclusion

In conclusion, it may be stated that sulfonation is a fairly simple procedure involving the use of easily available raw materials and simple design of equipment, and offering a variety of products of great value in direct use and as auxiliaries in many important industries, including the leather industry in which we are interested in this context. There should therefore be a very bright future for the same in India.

Acknowledgement

The author wishes to thank Prof. G. S. Laddha, Director, A. C. College of Technology, for permission to present the paper.

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Discussion

Mr. G. Lakshminarayana, C.L.R.I. : Is it advisable always to stick to the temperature obtained by theoretical calculations rather than suitably modifying it for practical purposes, for at the temperature suitable for sulphation, more resins are formed whereas at a higher temperature, dispersion occurs and good emulsion is obtained. Do the resins formed, interfere with the sulphation ?

Chairman, on behalf of the author : The processes are arranged in such a way that every reaction takes place at each stage. In industry if undesirable effects are produced, recycling could be resorted to.

INDIGENOUS FISH OIL FOR THE TANNER

BY

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ABSTRACT

The different methods of treatment of leather with oil have been enumerated with the mechanism of treatment. The importance of cod oil to the European tanner and the corresponding use of indigenous fish oil by the Indian tanner has been stressed.

The fish oil of West Coast at present contains too much of impurities rendering its use without refining very unsafe, especially if the treated leathers are to be exported to foreign markets where spewing troubles may be encountered.

The chemical characteristics of fish oils suitable for the different uses on leather are given, and the necessity of conducting research in the proper blending the fish oils of high iodine value with vegetable oils to evolve a good currying oil, has been pointed out. Mackay test determining the oxidisability of fish oil has been described in full with the importance of this test.

The duty, on the one hand, of the fish oil manufacturers to improve the quality of fish oil and increase the quantity by adopting modern techniques and on the other, of our Government to permit the free import of fish oil till the country attains self-sufficiency in this product is clearly brought out as otherwise the country cannot become self-sufficient in industrial leathers, in the near future, this oil being required imperatively for such leathers.

Oil is to be incorporated into leather in some form or other to make it soft, pliable and strong by lubrication of the fibre structure. In practice this may be effected either (1) by smearing oil on the moist tanned skin and allowing it to absorb the oil in the course of drying as in the case of vegetable tanned leather, (2) by treating the wet leather with emulsions of oils as in fat liquoring chrome tanned leathers, or (3) by introducing heavy grease mixtures (dubbin) into leather as in currying heavy leathers. Cod oil is the favourite of the European Tanners from very early days. It is believed that when cod oil is applied to leather, besides lubrication of the fibre structure by its deposition in between the fibres, the unsaturated character of the fatty acids of cod oil would help it to enter into some chemical combination with the protein structures and produce an oil tanned effect as well. Thus cod oil became very popular with the tanner for his currying and fat liquoring purposes besides its original use for chamoising. The Indian tanner is to depend on indigenous fish oils which are in some ways different from cod oil. Experience has shown that indigenous fish oils can be made suitable for successful use in leather manufacture by suitable adjustments in the extraction and purification processes.

Cod liver oil, shark liver oil and such other liver oils, are, as their very names indicate, extracted from the livers of the respective fish. Newfoundland cod oil which is most esteemed by curriers is thus prepared from the livers of cod fish, by steaming the more or less putrid livers—unsuitable for medicinal purposes—and rendering the residue by fire heat. As it is rendered at a higher temperature the albuminous matters precipitate out and the tendency of the oil to " spue " on leather is lessened. Whereas fish like the cod and shark have very oily livers and rarely have much oil in other parts of the body, in many other varieties of fish the largest yield of oil is from the body and the intestines. The Japanese sardine oil is extracted from the whole fish either by boiling or by allowing it to rot in heaps and subsequently pressing the mass. In South India, sardine oil is extracted in the West Coast, in a more or less similar manner, pressing cooked fish and collecting the oil. Skate oil is prepared in the East Coast of India from the livers of skate fish though in smaller quantities. Shark liver oil is too valuable to be available to the tanner and is used only for medicinal purposes.

These unrefined fish oils are quite unsuitable, as such, for quality work in leather manufacture, chiefly because of the presence of undesirable albuminous matter and the stearines. Further, although the oils are of very low acid value when freshly extracted, due to the presence of moisture and dirt, and the crude forms of storage, the rancidity of the oils increases rapidly resulting in high acid value, thus lowering the quality.

If these untreated fish oils are used for currying, the tanner has to experience the troublesome defect of " spue " or exudation of oil in an oxidised form on the surface of the leather. This defect is apparently due to some kind of fermentive change and is favoured by the presence of nitrogenous matter. It is also said to be most frequent with oils of a high acid value, due to the greater oxidisability of the free fatty acids than of neutral oils. So it becomes imperative that fish oil meant for the leather industry must be straightaway refined before storage. The high melting point stearines and the albuminous matter that separate out on standing or slow cooling of the oil—known in the industry as " foots "—must be completely removed by filterpressing or centrifuging after cooling the oils slowly to the required temperature.

Separation of high melting point stearines may be considered a problem of less importance in a tropical country like ours where the minimum temperature never goes so low as in temperate climates. The defect of spueing due to the solid fatty acids coming out to the leather surface will be greater in the colder climates. So even though centrifuging or cold pressing of our fish oil is not done as thoroughly or at such a low tempearture as in the colder countries of the West, there may be little trouble of spue as far as the leather is being used in a tropical climate. But the same piece of leather may show bad signs of spue if taken to the foreign markets where the climate is colder. So to be on the safer side, fish oil to be used for leather manufacture must be gradually cooled and filterpressed or centrifuged near the freezing point. An oil free from " foots " will be an asset to the Leather Industry.

It was already mentioned that the acid value of good quality fish oil must not be very high. A very high acid value—*i.e.*, the presence of a larger percentage of free fatty acids in the oil—is very unsuitable for oil tanning or chamoising. It is not that the free fatty acids by themselves are injurious to leather but being easily oxidisable than the neutral oils (triglycerides) as can be shown by Mackay Test, their action on pelt is a bit drastic resulting in a harsher leather. For chamoising, an acid value between 20 and 40 is preferred whereas for currying purposes better results are obtained with oils having acid values lower than 15. Freshly extracted fish oils have considerably low acid values and if refined by removal of foots, water and other dirt without any loss of time after extraction, any development of rancidity is checked thereby and the acid value of the oil can be kept at the minimum.

Fish oil has usually an Iodine value of 120 and above. Iodine value denotes the unsaturated character of the oils. Oils with higher iodine values (150/160) are suitable for chamoising purposes whereas those with lower values (120/140) are preferred for currying and fatliquoring. The sardine oil of the West Coast of India has a high iodine value (above 160). It should be a matter of considerable interest to the tanner to find out whether this oil can be blended with suitable vegetable oils of lower iodine value to adjust the iodine value of the blend to fall within the range preferable for currying purposes and how such a blending will affect the nature of leather produced.

The higher the iodine value, the more will be the oxidisability of an oil. Apart from the iodine value, determination of which gives an indication of the unsaturation of the oil, the ease of oxidation of the oil can be directly determined by a test designed by Mackay. A specified quantity of fish oil to be tested is teased with a fixed quantity of absorbent cotton wool, packed loosely in a gauze cage and dropped into a water-jacketed container when the water is boiling vigorously. A thermometer bulb is placed in the centre of the wool and the time required for the thermometer to reach 100°C is noted. Good chamoising oils reach 100°C in about 30 minutes. Thus the oxidisability of a sample of fish oil and thereby its suitability for chamoising or currying can be determined by the Mackay Test.

Recently the Government of India have tried to focus the attention of the Indian Tanner on the production of Industrial Leathers, by restricting imports and creating a favourable atmosphere for the local products. Fish oil being an important commodity required for currying or fatliquoring of such leathers, the tanner in India is badly in need of enough suitable supplies of the same. It is high time for the fish oil manufacturers of India to fall in line and take to improved methods of extraction and refining to meet the requirements of the tanner in quality and quantity. Meanwhile our fishing industry is still in its infancy with its outmoded methods. So the sources of indigenous fish oil are very unsteady due to the fluctuating type of the "catches." The aim of the Government of India to attain self-sufficiency in Industrial Leathers can materialise as soon as practicable, only if the tanner is active throughout the year ; and to augment our indigenous sources of fish oil—the steady supply of which, at least for the present, cannot be much relied upon—there is no escape from allowing enough imports of fish oil for our Leather Industry till our fishing industry and fish oil manufacturers can meet the demands squarely.

USE OF MODIFIED SUGARCANE WAX IN LEATHER POLISHING COMPOSITIONS

BY

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ABSTRACT

India is importing waxes like carnauba and montan worth about 10–12 lakhs rupees, for the manufacture of leather polishes, floor polishes, car polishes, etc. In addition to this, wax polishing compositions valued at Rs. 10 lakhs are also imported.

India has no natural source of waxes like carnauba wax. Sugarcane wax is the only indigenous wax which can be made abundantly available. The crude cane wax gives good gloss on application, but it has some major draw-backs like its dark colour, stickiness and poor solvent take-up property and therefore, has not much industrial use. As a result of the work carried out during the last few years at the National Chemical Laboratory, a process has been evolved which includes oxidation of the crude cane wax and chemical modification of the oxidized wax to obtain modified waxes. By this process it is possible to prepare, modified sugarcane wax which can be utilised fairly satisfactorily for the manufacture of leather polishes in place of carnauba and montan wax. The only drawback is that the creams prepared from this wax are a little softer above 40°C.

The above process for the modification of sugarcane wax and its utilization for the leather polishes are discussed.

The durability of the finished leather products and their attractiveness are dependant mainly on the quality of the polishing composition, such as leather cream polishes, liquid paste polishes and emulsion type of creams used for preserving leather goods.

India is importing waxes like carnauba and montan worth about 10–12 lakhs of rupees. In addition to this, ready-made leather compositions of nearly the same value are also imported.

As India is trying to be self-sufficient and attempting to reduce the demand for foreign exchange, it is essential to utilise if possible some indigenous product in place of the imported waxes for manufacture of polishing compositions.

In India if the cane wax is extracted from the press mud of all the sulphitation sugar factories, the total amount available would be about 10,000 tons of crude wax. We actually need only about 300 tons of hard gloss giving wax. Though we have this valuable source for the wax, the crude wax cannot be used as such in the industry. It has got a number of draw-backs like dark green black colour, stickiness and poor solvent take up property. Solvent take up property is very important from the point of view of getting hard creams and since carnauba wax possesses this property it is much valued in the industry.

The waxes used in the polishing composition are mainly of three types : (1) Gloss giving together with good solvent take-up property, *e.g.*, carnauba and montan, (2) Fillers—paraffin and ceresine and (3) binding waxes—waxes of the group of bees wax. Out of these three, waxes of the first category are very important and there has been urgent need to have a satisfactory indigenous substitute for waxes of this group. Such substitutes have not been so far prepared in India. India has enough supplies of the waxes of second and third category.

India has no natural source of waxes like carnauba or montan. Sugarcane wax is the only indigenous wax which can be made abundantly available.

The sugarcane wax gives very good gloss on application ; however, on account of its draw backs which have been pointed out earlier it cannot be used as such in place of carnauba and montan waxes.

Since 1952, we are carrying out systematic work on the sugarcane wax. The work can be mainly divided into three parts : (1) fundamental, relating to the constitution of sugarcane wax, (2) applied—bleaching and chemical modification of crude wax and utilisation of the modified waxes for different purposes and (3) isolation of sterols from cane wax. A general idea of the work on bleaching and chemical modification which has resulted in a satisfactory substitute for carnauba wax for use in leather polishes, will be now given.

Quite a good number of attempts have been made during the past by different workers to remove the colour and stickiness of crude wax. Some of the reagents tried earlier are inorganic acids, oxidising agents like potassium chlorate, hydrogen peroxide, organic solvents of the type of acetone, alcohol and isopropyl alcohol. However, none of these reagents was found to be satisfactory. The sugarcane wax was bleached with sodium or potassium bichromate and sulphuric acid. The bleached wax is obtained in 80% yield. This procedure removes the mineral matter, the colouring matter, and eliminates the unsaturation from crude wax. A part of the esters is hydrolysed and the fatty alcohols so formed are further oxidised to the corresponding long chain fatty acids. The bleached wax has got no solvent take-up property and can be used only for wax formulations like those of lipsticks and as a soap forming agent in polymerisation. The bleached wax is further converted into ester wax and amide wax by treating with glycols and diamines respectively. The amide wax has very good solvent take up property and yields hard creams. Mixtures of ester and amide waxes have been found to be suitable for preparing polish creams. These modified waxes give excellent gloss on application. We have tried to prepare creams from modified wax for testing the properties of the cream and also getting these tested by various firms. We have also given these samples to this Institute for testing. The reports received till now are satisfactory.

It may be of interest to know that, large quantities of basic chromium sulphate can be obtained as a by-product of the bleaching process, after proper treatment of the liquors.

We have also tried to prepare a simpler type of modified wax which has a good gloss and which can be obtained at a low cost. We feel that it could be used in emulsion type of creams and liquid paste polishes. The testing of this product is in progress at C.L.R.I.

Only a few uses of the modified waxes have been pointed out. In addition to these the modified waxes can be used in the preparation of floor polishes, car polishes, manufacture of carbon papers, mould releasing compositions, and for such other miscellaneous but important purposes. It is hoped that this information presented in short is enough to show the importance of the problem of manufacture of the modified sugarcane wax.

SUGARCANE WAX FOR SHOE POLISHES

BY

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ABSTRACT

Large quantities of sugar-cane wax, a byproduct of the sugar industry were being thrown away. Now, there is one plant operating in the United States (and another has probably started working in Australia) for the recovery and refining of the crude wax to obtain a hard wax possessing polishing properties. In India tens of thousands of tons of sugar-cane wax are still going to waste every year. The National Chemical Laboratory at Poona have developed processes by which the crude wax is bleached and modified chemically into different derivatives. Two of the hard waxes thus obtained were tried in shoe creams with good results.

Sugarcane wax is now looked upon as an important raw material owing to its potential availability. It is expected to become very useful. For example, it is conjectured[1] that specially processed wax derivatives will be got from the sugarcane wax similar to the very many synthetic waxes from montan wax (I.G. waxes). As the crude wax cannot be made use of as such, several modifications have been worked out. The modified form which is a hard wax can find use as a polishing material. It is suggested that the hard wax can take the place of Carnauba wax in shoe polishes.

Crude Wax : The crude wax is dark, sticky and odorous. It has poor solvent take up and retention.

Sp. Gr.—0.96–0.99 ; Acid value—4–12 ; Sap. value—40–57 ; Ester value—28–40 ; Iodine value—12.4 to 16.2 ; Acetyl value—55–95.

The characteristics vary according to source and extent of refining[2]

Modified waxes : The crude wax is subjected to further treatment. The following is a brief outline of the output and modifications worked out in different countries.

In America : From the sugarcane mills in the United States, Hawaii, Puerto Rico and Cuba about 30,000 tons of the wax go to waste annually. Nearly 19,000 tons of a dark hard wax could be produced from this crude wax which would exceed the world's production of Carnauba, Ouricuri and Candelilla added together.

At present there is one sugarcane wax plant at Gramercy, Louisiana (U.S.A.) operated by Colonial Sugars Co. The wax is refined by solvent extraction (acetone). The refined wax freed from resins and fatty oil is a hard wax melting at 76–79°C and consists of about 66% esters, 27% free acids, 5% free alcohols and 2% hydrocarbons. Chemically, the wax is more complex than other commercial hard waxes.

In Australia : A very different process has been evolved in Australia by H. H. Hatt. It is a three stage process consisting of :

(i) demineralisation with hydrochloric acid.

(ii) elimination of low molecular weight components by vacuum distillation.

(iii) bleaching with chromic acid.

A plant to process 1,000 tons per annum has been proposed and it is not known if it has already started functioning. The potential output of sugarcane wax in Australia does not exceed 2,000 tons.

In India : Probably one of the least exploited waxes in India is the sugarcane wax. From 12,000 to 45,000 tons of this wax (worth crores of rupees) are estimated[3,4] to be available as a byproduct from the Indian sugar mills every year. The National Chemical Laboratory have taken up this problem and have prepared several modifications[3,5] of the sugarcane wax, namely, amide wax, ester wax and etc., after first bleaching the crude wax with potassium dichromate and sulphuric acid.

Use of modified sugarcane wax in shoe creams

Samples of amide and ester waxes were obtained from National Chemical Laboratory, Poona. Several formulations of these waxes with other indigenous waxes were tried. It was found that a suitable blend of the amide and ester waxes would give rise to many of the desired properties like gloss, solvent binding and retention, adequate consistency and etc. The shoe creams prepared with the amide and ester wax blends along with other indigenous waxes are found quite satisfactory. Samples are being sent out for test reports.

Conclusion : Thus there is good reason to hope that sugarcane wax will become an important raw material for the shoe polish and other polish industries. The vast potential output of sugarcane wax from Indian sugar mills should offer enough temptation now for a full exploitation.

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NATURAL LATEX BASED ADHESIVE FOR LEATHER

BY

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ABSTRACT

Several adhesive compositions with rubber latex (Hevea brasiliensis) as the main ingredient were prepared and tried on leather. The experiments led to the formation of a latex-cement which has been found to be satisfactory. This latex cement is now being sold at Rs. 7 per imperial gallon (*i.e.*, Rs. 5.60 per American gallon) against orders from the local leather goods manufacturers.

Rubber, both natural and synthetic, has been used in a large number of adhesive compositions. The special properties of rubber which are found very useful in many of these applications are the high intitial tack and the high flexibility. As an adhesive, rubber has several advantages over the synthetic resins (especially the rigid types). In particular, it may be mentioned that when an attempt is made to rupture the adhesive bond, the high elasticity of the bonding film of rubber absorbs a good deal of the strain whereas a resin film would tend to suffer from stress concentrations. These properties illustrate how rubber is very useful as an adhesive for leather, a material which is quite flexible in itself.

The two common forms in which rubber is used are : (1) Latex, which is a natural colloidal dispersion of rubber in water and (2) solution of crepe rubber in a suitable organic solvent. The latex adhesive is slower in drying and has less tack when compared with dry rubber solution. But a much higher concentration and lower viscosity is possible in latices than in dry rubber solutions. It is needless to mention that latex, being an aqueous dispersion of rubber, is free from toxicity and flammability that go with organic solvents in the dry rubber solutions.

Synthetic latices from butadience have been reported to be inferior to natural rubber.[1,2] The tackiness of Neoprene latex (type 571) is said to be negligible.

Latex-based adhesives are used in joining shoe parts. In fact, Reiner[3] has reported that the main application of rubber latex outside the rubber industry is in the leather and leather goods industry as an adhesive.

Though natural rubber latex itself has good bonding properties, it is necessary to modify it by the addition of substances which will facilitate its application, enhance its adhesive qualities and stabilise or preserve or, in other words, ensure its qualities over a long period of time. Numerous are the additives that have been tried with this purpose in view. To mention only a few : starch, glue, gelatin, casein[4], blood albumen, water-soluble silicate ; calcium hydroxide, sodium phosphate ;[5] chromates and dichromates[6], fossil gum,[7] factice.[8]

Vulcanised latex is mentioned in patent literature and in several other places. With regard to the problem of adhesion there seems to be no advantage gained by vulcanisation, because, it is only the film of rubber that develops strength thereby and not the adhesive bond between the rubber film and the fibres, leather or metals.

In view of the aforesaid unique properties of natural rubber latex, an attempt was made in this laboratory to develop a leather adhesive using the same.

Formulation Experiments

Natural rubber latex from the plantations in Travancore was obtained in a concentrated and preserved condition. The latex was compounded with a large variety of substances severally and in certain combinations.

A few of the numerous substances tried in these formulations are : Carbonate and bicarbonate of soda, borax, chromates and dichromates, sodium silicate, sodium phosphate ; caustic soda, ammonia, triethanolamine ; glycerol, gelatine, glue, sulphonated castor oil, hydrogen peroxide, carboxymethyl cellulose.

The resulting products were tested for their adhesive properties. The strength of the joints prepared by using these adhesives was determined in the following manner.

Bond tests

Rectangular pieces of leather 5″ × 4″ were cut out from the butt portion of the finished sides. Prior to this the flesh side was buffed in the machine (the same grade of emery paper was used in all cases). After brushing off the dust thoroughly the adhesive was applied uniformly on the flesh side of the leather pieces by means of a brush. As soon as the brush coat airdried the two pieces of the leather to be joined were brought together and pressed together with a roller (one inch diameter). After airdrying for 24 hours, the joints were tested in a Scott Tester for obtaining the pealing load. The pealing load per inch width of the joint was taken as the adhesive bond strength. After performing series of experiments as indicated already, a formulation which has been found quite satisfactory has been arrived at. As it is intended to patent this invention the details of the experimental results are not given here. This latex adhesive is now being prepared in lots of several gallons in our laboratory. It is being supplied to the leather trade under the name of " latex cement " at a competitive price of Rs. 7 per imperial gallon.

With the experience gained in the above investigation, it is hoped to develop other suitable latex-adhesives to cover as many different applications as possible in the leather industry.

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COATED ABRASIVES IN LEATHER AND SHOE INDUSTRIES

BY

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ABSTRACT

The paper deals with the following : General ideas about coated abrasives ; Different types of grain and backing ; Manufacturing Technique ; Gravity and Modern Electrostatic coating ; Open and closed coats ; Flexing Process and Silky process ; Buffing of leather ; Grain side and flesh side—use of flint, silicon carbide and aluminium oxide abrasives ; Different types of buffing machines ; Abrasives in Shoe Industry : Use of glass paper and flint paper for hand sanding and use of garnet and silicon carbide paper and cloth combination materials in machines.

Modern coated abrasive is an essential tool in present day production methods. Without it, the fine finishes, interchangeable parts and precision workmanship required for mass production would be seriously handicapped. This is particularly true of leather industry where without the aid of modern buffing papers it would not be possible to produce in quantities the high quality leather required for consumer goods such as shoes, hand bags, etc., The finish called for by the modern tanner is so critical that even a slight scratch, almost invisible to an untrained eye, left on the finished leather meets with his disapproval, Origin of coated abrasives is lost in antiquity. While the coated abrasives in the modern form were developed only during the last hundred years, it is known that in the middle ages, dried fish skins were employed for smoothing furniture. About the beginning of 19th Century, pumice was mixed with varnish and coated on paper with a brush. Early method of getting different grades of emery paper was to blow powdered emery into a chamber in which glue coated sheets were hung at various heights, the highest paper receiving the finest dust.

The modern coated abrasive consists essentially of three components : (*a*) Grain, (*b*) Backing and (*c*) Bond.

Grain

Five different qualities of grain are used :

Flint, *i.e.*, powdered quartz, Garnet, *i.e.*, a mixed silicate of Ca, Mg, Ferrous iron, Mn, Al, Ferric iron and Cr, emery, consisting of an intimate mixture of blue corundum with magnetite and also haematite, aluminium oxide and silicon carbide; while the first three are mined from earth's surface, the fourth one is product of electric furnace, manufactured by fusing purified bauxite ore with the addition of coke and iron under controlled conditions at temperature exceeding 3600°F, and the fifth one is produced by reacting silica with carbon in an electric furnace with the addition of sawdust and salt at temperatures upto 2400°C.

Characteristics of these grains measured in terms of hardness, toughness and fracture vary considerably making each grain suitable for certain application.

Flint has the least hardness and toughness but being splintery, fractures with sharp wedges. Garnet is next to flint in hardness but is much tougher but less splintery and so is aptly suitable for mechanical sanding of wood and other soft materials. Emery is harder and is very much tougher but is cubular and fractures with round and blocky wedges. Aluminium Oxide is next only to silicon carbide in hardness but is tougher and fractures with heavy wedges making it ideal for grinding steel and high tensile metals while silicon carbide due its extremely hard nature and with its ability to fracture into crystals with sharp and slivery wedges is well suited for grinding soft materials such as leather and low tensile metals, cast iron, etc.

Backing

Backings used for coated abrasives can be classified under three headings :

(*a*) Paper : Light weight paper is used mainly for hand sanding and for light mechanical applications such as on vibrating sanders.

Heavy weight paper is used for mechanical application usually in the form of rolls as in buffing or as belts.

(*b*) Cloth : Drill backing for applications where backing stronger and more flexible than paper is required.

(*c*) Combination :

(*a*) Heavy weight paper combined with light weight cloth. This product is stronger than paper and less expensive than drill cloth and is used where the stress and strain is greater than what the paper is capable of standing. It will resist stretch better than cloth but has no flexibility at all.

(2) Cloth combined with vulcanised fibre. Mostly used for manufacture of abrasive discs for use on high speed sanders.

Bond

(*a*) Glue, (*b*) Resin and (*c*) Varnish.

Most of the abrasives are of glue bond but where high heat resisting property is required resin bond is used.

Varnish is used only for waterproof abrasives.

Manufacturing Process

There does not, at first sight, appear to be any necessity for complicated manufacturing technique and machinery to produce coated abrasives. But when it is realised that coated abrasives are required to produce repetitive finishes day in and day out to meet the exacting demands of all industries, extensive control and elaborate apparatus become an absolute necessity.

Two methods of coating are employed each using much the same layout. The first method which is the older method but still quite prevalent especially for manufacture of abrasives such as flint and emery for hand application, is the gravity coating. In this process, the backing, either paper or textile, is given a coating of adhesive by passing it through rollers dipped in a trough of adhesive and grain is dropped from a hopper on to it by gravity. After partial drying, another layer of adhesive called sizer coating is given to the abrasive after which it is dried under controlled conditions and finally wound into rolls for further processing. The disadvantage of this process is that abrasive particles lie haphazard on the surface, as they happen to fall, with many of their keen cutting edges lying flat or even embedded in the adhesive layer.

In order to rectify this defect, the other type of coating called " Electrocoating " is employed. In this process the abrasive grains are carried into an electrostatic field created by high voltage equipment (from 25,000 to 60,000 volts both AC and DC) and are given a negative charge while the adhesive coated backing moving above the conveyor is positively charged. Under the electrostatic field, each abrasive grain orients itself along the line of force of the electrostatic field, *i.e.*, it literally stands on end. The voltage is so adjusted that the electrostatic field is powerful enough to make the grains travel upwards so that they get embedded in the adhesive layer along the broad sides which possessess maximum charge. This results in an absolutely uniform coating with sharp edges of the grains sticking out and broad bases firmly anchored in the adhesive layer. Hence these electrocoated abrasives cut faster and cooler, last longer, clog less and remove much greater stock.

The coated abrasives wound in the form of rolls after drying are allowed to 'age' in a conditioned atmosphere. These rolls are later fabricated into required shapes such as sheets, rolls, belts, discs, caps, etc.

Strict quality and technical controls exercised at every stage of manufacture beginning with raw materials and ending with finished products ensure that all the commodities are manufactured correctly according to specification so that the consumers are assured of the absolute uniformity in quality, There are two types of grain coating : (1) Closed coat and (2) Open coat.

As the name itself implies, in closed coat, the entire surface of backing is completely covered with grain. In open coat, 50 to 70% of the backing is covered with grain. With greater spacing or void between, open grain coating allows the material sanded to free itself without filling or clogging the surface.

An important treatment given to coated abrasive to increase its flexibility is the " Flexing " process. The coated abrasive as it comes off the machine is fairly stiff and for operations where greater flexibility is required flexing is carried out to the desired degree. Two types of flexing are employed called 90° flex and 45°flex. 90° flex gives a material that is flexible in the lengthwise direction. This is accomplished by passing the material over a narrow bar at right angles to the length of the material which breaks the bond across the width. For flexing diagonally across the material to obtain 45° flex, the materials are taken over similar machines but fitted with two flexing bars set at right angles to each other and at 45° to the edge of the roll. It is of importance to note that flexing reduces the durability of the abrasive and as such it is desirable to select abrasive with minimum flexibility consistent with the grinding job. One other advantage in flexing materials is that the backing gets prestretched to a certain extent so that stretching of the abrasive during use on a machine is reduced considerably.

Buffing of leather : For the leather industry, the accuracy of grit size, uniform grain coating and sharp cutting abrasive are of greatest importance. Silicon carbide is the most popular abrasive for buffing of leather. In addition to being the hardest of all abrasives, it fractures into crystals or grit sizes with the longest edges and best dished shape or concave sides, of all the other materials. Its use is only limited due to its relative brittleness. Its sharpness cuts into the soft yielding surface of the leather freely without pulling or tearing and the life of the abrasive is quite satisfactory since the leather itself is not resistant enough to break it down.

However aluminium oxide abrasive is becoming increasingly popular. This is more due to the development of modern high speed buffing machines. Aluminium oxide grains though not having the very sharp wedges or hardness characteristic of silicon carbide are much tougher and are able to stand high speeds and heavier pressure. Even for low speed machines aluminium oxide is preferred for certain types of leather mainly for buffing of grain side where silicon carbide might tend to produce scratches.

A special process called ' Silky Process ' has now been evolved by Carborundum Universal for producting buffing papers both in silicon carbide and aluminium oxide required for practically scratch free finishes on leather.

Flint abrasive also finds a limited use for buffiing due to its being softer than either aluminium oxide or silicon carbide and provides the correct medium for superfine buffing of certain types of leather such as calf or glazed kid. However, the life of flint abrasive will be very short.

Backing used for buffing abrasives is mostly the heavy quality paper. For more severe applications, particularly when the paper is liable to tear or peeling of grain with portion of the ply of paper is experienced, cloth backing has been found to be useful. However, since the cloth backed abrasives are costlier than the paper ones, economy of the process should be properly studied before introducing cloth backed abrasives for leather buffing.

Buffing machines can be broadly classifed into two types :

(1) Low speed machines with radial or spirally wound papers on cylinders which may or may not have oscillatory motion in addition to rotary motion. The oscillating movement of the rotating buffing cylinder vastly improves the quality of the grinding effect. The advantage of spiral winding over the normal radial clamping is that it reduces wear and tear of the abrasive paper, produces uniform buffing and avoids chatter marks due to continuous winding of the paper over the cylinder, (there is no straight line break at the portion of the clamp) and increases output due to increased working width of the spiral band cylinder.

(2) High speed buffing machines of the type of "Lightning" buffing machine of Turner make. The high speed increases the output considerably while enabling lighter pressure to be applied on the leather. The working width is larger enough to pass a whole skin or side through the machine which consequently produces an uniform finish in one stroke.

Abrasives in shoe industry : Coated abrasives play a very important part in shoe manufacture. While the upper leather is received in finished condition after being tanned, buffed, and dyed, all the other parts of the shoe such as soles, insoles, and heels are required to be sanded. The old method which is quite prevalent still in India is hand sanding using glass paper wrapped round rectangular wooden sticks. It is not adviasble to use glass paper due to the extremely brittle nature of glass grains which produce dangerous dust that is injurious to the health of workmen using this paper. Flint paper can be more advantageously employed for this purpose.

The latest method is to use machines fitted with modern coated abrasives. The operations involved can be divided into two heads :

(1) Initial and (2) Final finishing.

Buffing of insoles, heel stiffeners or counters and roughing of soles, shoe bottoms, etc., constitute the initial process. Buffing of insoles is now done on a belt grinding machine employing open coat garnet or silicon carbide abrasive. Roughing of soles or bottoms is conveniently carried out on small cylinder wrapped round with flint, garnet or silicon carbide abrasives of very coarse grits. The backing required for these coarse grit abrasives is heavy weight paper or combination of paper and cloth. While flint and garnet are satisfactory for low speed machines, silicon carbide is required when the speed is high.

Finishing operation consists of heel scouring, heel breast scouring and buffing of shanks. For scouring of heels, silicon carbide or garnet abrasive on paper or combination backing are used in strip forms which are mounted on felt covered wooden or aluminium wheels. Heel breast pads in the form of truncated cones mounted on conical heads are employed to sand the breasts of the soles which are easily sanded by the scouring coils. Naumkeag caps made of silicon carbide cloth are very useful for sanding the bridge of the soles called shanks. Mounted with foam rubber pads on high speed vertical spindles they enable one to sand the soles in a fraction of the time required otherwise for the laborious hand operation.

For all sanding operations on shoes, it can be summed up that garnet is satisfactory where low speed machines are used and that silicon carbide is definitely warranted when the speed is high. Flint can be advantageously be used in coarser grits for light roughing operations. While paper backing is normally sufficient, for extra coarse grits combination backing would be necessary.

The pattern of trade in Hides and Skins and Leather Industry in India is undergoing a gradual change. We find that more and more people are taking to manufacture of leather products within the country itself instead of merely exporting raw Hides and Skins. This is a welcome development and our Company, M/s. Carborundum Universal Ltd. are endeavouring to serve the needs of the Leather and Shoe Industry in the country to the best of their ability by making available supplies of the right type and quality of abrasives and by extending such expert technical service as is required. The author would earnestly appeal to all to feel free to indent on assistance from them with regard to abrasive problems.

The author is obliged to the Organisers of the Leather Auxiliaries Symposium for having given him this opportunity to speak to such a select and distinguished gathering of members of the Leather Industry.

A COMPARATIVE STUDY OF THE MECHANICAL PROPERTIES OF CHROME RETAN UPPER LEATHERS

BY

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ABSTRACT

The tensile strength, elongation, tongue tear strength, double hole stitch tear strength, grain crack strength, bursting strength and stiffness factor of light and heavy chrome retan leathers are compared. It is found that chrome retan stuffed leathers possess better mechanical properties than chrome retan fatliquored leathers. The order of merit from the point of view of the mechanical properties is arrived at for chrome retan light leathers ; Myrob and Quebracho are first, followed by Gambier and Wattle, while Cutch occupies the last place.

Introduction

In the course of an investigation of the inter-relationships between the mechanical properties of chrome retan upper leathers, some interesting results were obtained using light and heavy leathers of different retannages and of different after-treatments. As these results may be of value to the leather industry, they are presented in this paper. The number of samples on which these results are based was not as large as may be desirable ; however, the general trend of variation of the properties with the different retannages or after-treatments is indicated.

Experimental

The cow hides used in the investigation were treated in the following ways :

In the case of light leathers, all the hides were first tanned with chrome in the usual way and then with one of five different vegetable tannages (10% extract), *viz.*, Cutch, Quebracho, Myrob, Wattle and Gambier. Heavy leathers were given the following treatments after an initial chrome tannage : (*a*) Cutch retannage and soap fatliquored, (*b*) Cutch retannage and fat-liquored with sulphonated Pongam oil and free Pongam oil, (*c*) Cutch retannage and hand stuffed, (*d*) Quebracho retannage and hand stuffed, (*e*) Cutch retannage and double bath fatliquored (*f*) fatliquored, and (*g*) hand stuffed. Two of the samples were only chrome tanned and treated as at (*f*) and (*g*) for purposes of comparison, The test samples were obtained from a block (11″ × 9″) situated at a distance of 2″ from the backbone line and 4″ from the butt end, the longer side of the block being perpendicular to the backbone line. Within the blocks, the samples for the various tests were cut out from identical regions to eliminate locational variations in the properties. A Scott Tensile Strength tester was used for tensile strength, elongation, tongue tear strength and double hole stitch tear strength, a Mullen tester for grain crack and bursting strength, while the stiffness factor was obtained by the use of a Tinius Olsen Stiffness tester of 6 inch-pound capacity. Details of these tests have been described elsewhere.[1] All the samples were conditioned for well over a week at 80° ± 4°F. temperature and 65 ± 2% relative humidity.

Results and Discussions

A comparison of the mechanical properties of chrome retan fatliquored, chrome retan stuffed, chrome fatliquored and chrome stuffed leathers is made in Table 1. Table 2 gives the average values of the properties for light leather and Table 3 the order of merit for the various retanned light leathers from the point of view of the mechanical properties. In the tables, a higher stiffness factor indicates less flexibility.

It is seen from the results of Table 1 that chrome retan stuffed leathers have better mechanical properties than chrome retan fatliquored leathers. Comparing chrome retan stuffed and chrome stuffed leathers, chrome leathers are better excepting for tensile strength and grain crack. The mechanical properties of chrome fatliquored leathers are better than those of chrome retan fatliquored ones. It may also be seen that the shrinkage temperature of chrome retan stuffed leathers is higher than that of chrome retan fatliquored leathers and chrome fatliquored leathers have a higher shrinkage temperature than chrome retan fatliquored leathers. A higher shrinkage temperature would thus appear to indicate better mechanical properties. This is understandable in the case of most of the mechanical properties studied in this paper excepting stiffness factor where a higher shrinkage temperature is associated with greater flexibility in the case of chrome retan leathers. However, no generalisation could be made here with regard to the relation between the shrinkage temperature and the mechanical properties as, in the other cases, *viz.* light leathers, the shrinkage temperature is more or less the same while the mechanical properties are different. A study in terms of the properties of the constituent fibres and the structure of the leathers appears necessary before a generalisation could be made in this regard.

Turning now to the chrome retan light leathers, the order of merit for the various retannages is given in Table 3. This order, which differs according to the mechanical property considered, is based on the results shown in Table 2. The order is quite clear in the case of elongation, tongue tear strength, double hole stitch tear strength, grain crack and stiffness factor. In the other properties, *viz.*, tensile strength and bursting strength, the differences between two consecutive tannages are not significant. At the same time it is not possible to group all of them together because the differences in the values between the alternate tannages (*e.g.*), Nos. 1 and 3, and 3 and 5 are considerable. The orders given for these properties have, therefore, this limitation.

It is also seen from Table 3 that the order of merit is different for the different properties *e.g.*, Cutch is ranked first for stiffness factor but is third for the tear tests. Again, in order for the stiffness factor, the stiffest is ranked first. Whether stiffness or flexibility is the desirable property depends on the use to which the leather is to be put. The same remark holds good for elongation. If the leathers are to be used for shoe uppers, the most important properties are double hole stitch tear, grain crack and flexibility. The order for the stiffness factor has, therefore, to be reversed and it will read (1) Quebracho and Gambier. (2) Myrob. (3) Cutch and Wattle.

Looking at these retannages from the point of view of shoe uppers, therefore, one might strike a balance between the properties and arrive at an order as follows : (1) Myrob and Quebracho. (2) Gambier and Wattle. (3) Cutch.

It may be mentioned here that the difference between grain crack strength and bursting strength is very small in some cases, *e.g.*, chrome retan stuffed leathers, while in other cases, (e.g.) chrome stuffed leathers, this difference is large. This may be attributed to the strength of adhesion between the grain and corium—a weaker adhesion resulting in a greater difference between grain crack strength and bursting strength.

A detailed explanation for the differences in the properties can no doubt result only from an elaborate investigation of the fibrous architecture of the leathers and the molecular architecture of the fibres themselves.

ACKNOWLEDGEMENTS

The authors have great pleasure in recording here their sincere thanks to the Control Laboratory and the Tanning Division for supplying the samples and the Director, Central Leather Research Institute, for permission to present this paper at this symposium.

REFERENCE

[1] N. Ramanathan and D. V. Subbalakshmi : *Proceedings of the I.S.I. Convention,* 1957, Session T.-7, Document AP 19.

TABLE 1

Comparison of the Mechanical Properties of Chrome Retan Heavy Leathers

	Tensile strength (lbs./sq.in) (a)	Elongation at break (Percent (b)	Tongue tear (lb./inch) (c)	Double hole stitch tear (lb./inch) (d)	Grain crack (lb./sq. in/ inch) (e)	Bursting strength (lb./sq. in/ inch) (f)	Stiffness* factor (lb./sq.in.) (g)	Shrinkage temperature °C (h)
Chrome retan fatliquored	3,000	33	78	600	7,000	10,100	700	114
Chrome retan stuffed	3,550	41	90	730	10,800	11,900	580	120
Chrome fatliquored	3,470	38	150	1,000	...	18,400	570	118.5
Chrome stuffed	3,330	53	157	920	6,000	12,300	410	120.5

TABLE 2

Mechanical Properties of Chrome Retan Light Leathers

10% *Extracts :*	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)
Cutch	3,110	30	85	610	7,300	11,100	970	112.5
Quebracho	3,030	32	102	650	10,300	12,500	680	112.5
Myrab	2,620	36	125	920	9,600	13,500	850	110
Wattle	2,770	32	118	720	9,400	11,700	1,030	112
Gambier	3,250	31	78	720	8,000	9,900	690	112.5

TABLE 3

Order of Merit for Chrome Retan Light Leathers

(a)	(b)	(c)	(d)	(e)	(f)	(g)
1. Gambier 2. Cutch 3. Quebracho 4. Wattle 5. Myrab	1. Myrab 2. All others	1. Myrab and Wattle 2. Quebracho 3. Cutch and Gambier	1. Myrab 2. Wattle and Gambier 3. Cutch and Quebracho	1. Quebracho, Myrab and Wattle 2. Cutch and Gambier	1. Myrab 2. Quebracho 3. Wattle 4. Cutch 5. Gambier	1. Cutch and Wattle 2. Myrab 3. Quebracho and Gambier

*The length of leather bent was ½" ; angle of bend 30° for heavy leather and 50° for light leather.

Discussion

Mr. S. K. Mitra (C.L.R.I.) : Could comparative data for chrome tanned and chrome retanned leathers be given?

Dr. Ramanathan : Certain properties like stitch tear strength, grain crack, stiffness factor, have been studied with chrome fatliquored leather and chrome-retanned fatliquored leather. However, the results do not establish conclusively overall superiority of one over the other.

THE APPLICATION OF QUALITY CONTROL TO LEATHER RESEARCH AND INDUSTRY

BY

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ABSTRACT

The possibility of applying Quality Control techniques, to Leather Research and Industry, with advantage has been reviewed. Also the difficulties that may be encountered while applying the quality control techniques are given with some suggestions to overcome the same.

Industrial development is a stepping stone towards the advancement of civilisation. With the application of scientific knowledge gained through the passage of years and painstaking research, it has become possible for the industrialists to manufacture the various goods needed by the modern society at a considerably low cost. Nowadays, if a producer has to thrive in the competitive market, he must be able to produce goods of an acceptable and standard quality at an " optimum cost." To produce such a commodity, statistics has become a very useful tool in the hands of the modern industrialist.

What is Quality Control ?

We are all aware of the fact that reputation for uniformity and dependability of quality of output is in many cases one of the most important assets of a concern. For a given kind of product, the manufacturer sets a standard for the quality and thus he tries to make all batches of the product conform with this standard. In the practical field, it may not be possible to produce batches all alike because there are several " chance variations " operating at all stages of the manufacturing process. So he would set up a standard which is not an absolute constant, but variable within limits. To be precise, phenomena will be said to be controlled, when through the use of past experience, we can predict at least within limits, how the phenomena may be expected to vary in future.

In the application of Quality Control to any industry, the manufacturer should set up clearcut standards to be used in measuring the quality of a given kind of product ; unless definite quality standards are carefully worked out and formulated, the measurement of quality becomes a matter of human judgment with the possibility of ' chance causes ' and as such the quality will suffer and the standardisation of quality would be of little avail.

How to prescribe the Quality Standards ?

Before applying Quality control standards, the degree of quality desired or needed is always the primary consideration. It is not always correct to say that the goal to strive for always should be the highest quality. It is much better to determine carefully just what quality requirements are feasible in terms of cost of production, the use to which the product is to be put, and the price in the competitive market. To be more exact, the primary consideration of any business concern is the quality/cost ratio *i.e.*, to obtain better quality at a comparitively lower cost. Upon the basis of such consideration, the quality standards should be prescribed and worked out.

Control of the process : After setting up the quality control standards, the next thing that one has to do is to check the quality of the product at the various stages of manufacture and to rectify the defects if any, if the process has gone out of control.

In practice, however, it is either impossible or impracticable or uneconomic to control all the conditions precisely. Raw materials of biological origin cannot be made uniform. It is also impossible to eliminate entirely the human factor involved in the manufacturing process. All these sources of variations are natural to the process, and since we have to put up with them, we may describe the resulting variations in quality as " allowable or chance causes." Sometimes, when the process goes out of control, we can find the cause and these are termed as " Assignable causes." These may be detected and eliminated.

In the control of a process, it is very necessary to check the product under manufacture at each stage. Since the quality of the final product emerging out of the manufacturing process depends primarily upon the quality of the raw materials, it is particularly necessary for the quality control section to use standard raw materials at an " average cost." It is also necessary to prepare ' control charts ' for various stages and care should be taken to see that during the process the product conforms to the standards specified in the charts within the practical limits. In order to eliminate the inevitable shortcomings of the human factor, the application and the use of machinery may be standardised in the best manner possible. If during the manufacturing process, the product does not conform to the standards specified in the control charts, then the defects should be rectified and if it is not possible, it is better either to reject the product under consideration or process it for a low variety finished product.

Inspection and certification : After the product is manufactured, in the manner described above, it is to be tested, whether it conforms to the standards specified before it is let out to market. In certain cases (*e.g.*, bulbs, telephones etc.) a 100% inspection would be necessary ; in other cases depending upon the degree of quality desired, the tests are to be conducted. For conducting the tests, it is necessary to adopt random sampling or stratified random sampling without any bias whatsoever. The tests are to be carried out under standard conditions and the apparatus for testing should also be standardised.

After the testing is over, the product is certified for the quality and those which do not conform to the standards specified are rejected as low quality.

Advantages of applying Quality Control

Dr. Shewart has clearly enunciated the advantages of a successful application of Quality Control techniques to our industry. He is of the opinion that through a state of control we can secure the following advantages :—

(i) Reduction in the cost of inspection—assignable causes of variability are all removed during the control of the process at each stage.

(ii) Reduction in the cost of rejection : Defects are rectified during the process of production.

(iii) Attainment of maximum benefits from quality production .

(iv) Attainment of uniform quality even though the inspection test is destructive.

(v) Reduction in tolerance limits when quality measurement is indirect.

Besides the above, since quality products are standardised, the following advantages are also met with.

1. It helps to secure uniformity of products and methods of operation.
2. It provides a definite basis for analytical comparison and effective measurement of the tasks involved, and thus enables the management to maintain a close grip on production which is so very essential to efficiency.
3. It renders easy the work of constant improvements in processes and products so as to meet the varying needs of the market.
4. It helps towards regularised training of personnel, distribution of tasks and the establishment of a satisfactory system of enumerating labour.
5. With standardised products it is possible to have a constant demand in the market, due mainly to the reputation for quality and thereby remain unaffected by economic fluctuations.

Leather Industry and its problems : In modern economic organisation, the advantages and importance of quality control, are well apparent. The leather industry which is one of the major foreign exchange earners of our country may be suggested to be amenable to the quality control techniques. But in that case, the problem is not whether quality control techniques can be applied, but how it may be applied.

Raw materials : Hides and skins are the principal raw materials of the leather industry. They are biological in origin and as such vary in properties due to breed, origin of the animal, its mode of life, its food, general conditions, age, sex and nature of death. These have a very great influence on the process of leather manufacture. Also the hides and skins are obtained only as by-products and as such the tanner has no control over the prices as well as the quality. In India, the problem is more complicated mainly due to the fact that they are obtained mostly from fallen animals, *i.e.*, animals which have met with natural death. Due to defects in the method of collection, flaying and curing of the hides and skins, the gradation of the raw material according to their quality has become a practical problem.

In introducing the quality control techniques in the leather industry, it is essential to eliminate the defective raw materials (with damage due to warble, ticks, flay cuts, brand marks, fence wires etc.) as rejection quality to be used for low quality products. Assortment of the selected raw material may be made on the basis of their weights, area, type of cure employed, origin and nature of death if known. An assortment based on the combination of these factors will be of great avail. Hence it is desirable to grade the raw materials, assign the lot to different products (such as belting, sole, picking band etc.) depending on their quality.

Application of simple tests on raw materials

As regards the physical and chemical composition of the hides, it is complicated due mainly to the lack of uniformity in composition from place to place in the same hide and from hide to hide. Also hides are bought by weight and as such the amount of water abstracted and the mineral matter introduced during the process of curing is an important factor to be reckoned with. There are also practicable limits which are allowable to the proportion of mineral matter to hide substance in a dried hide. The proportion of moisture content and salt to hide substance in salted hides, is an important factor which arrests our attention and this quality may be considered as a basis for the gradation of hides.

It is also necessary to control the various processes involved in the manufacture as otherwise the gradation of raw materials according to quality would only be of academic interest. In the manufacture of leather, the cured hide is washed and soaked in water. Water has got a very great influence over the various processes involved in the manufacture of leather and if it is not standardised, leather would be of varying and low quality and this would be a cause for the loss of considerable revenue—(*e.g.*, lime blast, wastage of tannins due to precipitation etc. wastage of dyes due to precipitation etc.) The analysis of water is of practical importance to the tanner and it is the duty of the control section to see as to whether the water available in the tannery conforms to the standards specified for the requirements for different processes. If soaking agents are to be used, it is necessary to control the concentration, and also their percentage based on the weight of hide.

After soaking, in the liming operation, it is necessary to know the " CaO " content in the sample of lime used as otherwise there is every likelihood of wastage of lime. Also it must be made sure that the lime used is free from undesirable and detrimental impurities. In liming, the sharpening agents, if used, must be of a standard quality and their percent used must also be controlled.

In the deliming process, the various deliming agents used must also be analysed and this would throw more light upon the " optimum " amount to be used for various deliming processes. In bating and pickling also a correct analysis of the materials used, and also a strict control of time of treatment, will be of immense use.

Delimed pelt, is put into a mellow tan liquor for tanning. Here it is essential to find out and control the pH, the T/NT ratio, acidity etc. and optimum conditions should be worked out and strictly controlled.

" Quality tanning " materials should be used to have a perfect control over the tannage. By " Quality Tanning Material " it is meant that it is a tanning material of an assured T/N.T. ratio, acid salt content, and a definite pH. The colour is also of importance. Researches should also be carried out to find out the optimum time and conditions of tannage for different types of leathers.

During the process of drying and oiling a uniform method should be adopted. If the finances of the factory permit, then a drying chamber of controlled humidity and temperature (at all seasons) would be of advantage in controlling the drying rate. In short, all the accessory materials used should be of uniform and standard quality.

Final product

After the manufacturing process is over, it is but essential to see as to whether the produced product conforms to the standards specified for that particular type of leather. In specifying the standards it is necessary to bear in mind the use to which the leather under consideration is intended. For instance, in the case of sole leather, more importance should be laid upon the abrasion resistance value, apart from other physical and chemical characteristics. Similarly, in the case of picking band leather, more importance may be given to the tensile strength measurements.

In the testing of the final leather, it is uneconomical to have a 100% inspection as this would mean a considerable loss of revenue. Here, in testing and analysis of final product stratified random sampling method may be adopted to suit our quality requirements.

Difficulties that may be encountered in applying Quality Control techniques to the leather industry in the present set up

1. In India, there are more than 400 tanneries, turning out different types of leather intended for a variety of uses on a small scale. The capital outlay per tannery is limited and as such it may be argued that the application of the quality control techniques would be of little use as this may involve some additional expenditure. To overcome this difficulty, it is here suggested that leather co-operative societies may be set up (on the lines of the milk co-operative societies of Denmark).

2. *Lack of scientific personnel :* This is not a serious problem today because there are many institutions, turning out a number of scientists and technologists suited for the leather trade. These personnel may be specially trained for effecting quality control techniques. It is of utmost importance on the part of the industry to recognize the real worth of the technologists and to avail the services of the well trained technologists for the betterment of the industry in general. It is gratifying to note that at last the industrialists are recognizing the intrinsic worth of technologists and are employing them in their tanneries.

3. *Difficulties in specifying the standards and in preparing control charts during the manufacturing processes for different leathers :* It is well known that India is a sub-continent, the climate and other conditions varying widely from region to region. This factor may make it difficult to prepare a single control chart applicable to all the regions. Hence it is suggested to set up regional control laboratories which would work out different controlling factors in the process of a particular type of leather, according to the local conditions prevailing in that region. In India there are five important centres namely : (i) Kanpur, (ii) Calcutta, (iii) Bombay, (iv) Madras and (v) Madhya Pradesh and the regional laboratories can be set up at these places.

During the early postwar years, there was a complaint from the British importers that the Indian leathers (Half tanned E.I. leathers) were adulterated and as such they offered a lesser amount than their promise, and this led to serious business set back resulting in the closure of many E.I. tanneries. In order to have a command over the export market, it is very essential to set up an autonomous body which would test the sample of leathers to be exported and would certify to their quality. This, it is hoped, would go a long way in not only expanding our export market, but also in having a constant demand from countries which are already importing Indian leathers. In addition to the above advantages, the byproduct industries (like glue, gelatin, leather board etc.) can also be started which may bring in more revenue which would have been otherwise lost.

From all the above considerations, it can be seen that quality control may play a dominant and useful role in the future of this great industry.

ACKNOWLEDGEMENT

Sincere thanks are due to Dr. S. K. Barat for the valuable advice given by him to the authors in writing this article. Thanks are also due to the Director, Central Leather Research Institute, for permitting the authors to present this at this Symposium.

Chairman's concluding remarks : One of the most important problems in this country is the lack of proper leather auxiliaries. Further, the composition of the products obtained from the trade does not correspond to the theoretical standards, *e.g.*, in the case of petroleum products, a well-defined knowledge regarding chlorination, sulphation, sulphonation, hydrocarbon chain length etc., is not available. The petroleum products could be analysed and classified in terms of properties like detergency, wetting, emulsification, penetration etc. Similarly, in a fatliquoring process, the effects of sulphur, phosphorus could be studied.

He was however surprised that there should be a plea for import of fish oil when it was possible to manufacture the required variety in the country itself. The papers on sugar cane wax were interesting and it would be advantageous if such waste products and byproducts could be profitably utilised. With lignite deposits available in plenty, it should be possible to get montan wax also. The remaining papers were interesting and each was valuable in its own way.

Mr. R. Selvarangan proposed a vote of thanks.

PROCEEDINGS OF THE CONCLUDING TECHNICAL SESSION

Monday, the 17th March, 1958—Forenoon

Chairman : Mr. Nazir Hussain, Perambur Chrome Tannery, Madras.

Recorder : Mr. A. Ganesan, Central Leather Research Institute.

Mr. A. Ganesan introduced the Chairman.

The Chairman, in his opening remarks dealt with certain aspects of the leather industry needing immediate attention.

The quality of hides was deteriorating due to ban on cow slaughter. So the manufacture of first-class leather from poor quality hides was a big problem. It was in this context that the leather auxiliary manufacturers played an important part. To some extent, Central Leather Research Institute was solving problems concerning this aspect.

There was keen competition from plastics. So new finishes in bright and fast colours were needed and there was also a demand for water proof colours.

Actually the sole leather tanner was not happy because plastic replaced leather soles to the extent of more than 50%. However, upper leather had not been displaced by plastics. Leather could maintain its supremacy only with the help of the scientists. However, the future for the leather industry was as bright as ever.

He then announced the formation of a Leather Auxiliaries Drafting Subcommittee composed of the following members for making suggestions *vis-a-vis* manufacture of leather auxiliaries.

(1) Shri E. S. Subramanian, Handymen Industries Private Ltd., Madras.
(2) Shri U. A. Menon, Gordon Woodroffe Leather Mfg. Co., Madras.
(3) Shri J. K. Kothari, Lakshmi Tannin Extract Factory, Kharagpur.
(4) Shri T. V. Jagadeesan, Standard Vacuum Oil Co., Madras.
(5) Shri N. Viswanathan, Chemicolour Ltd., Calcutta.
(6) Dr. S. K. Barat, Central Leather Research Institute, Madras.

Papers were then presented in the following order :—

Pigment finishes for leather ...	Read by Mr. E. S. Subramanian.
Nitro-cellulose solvents and diluents-Types and Use.	Read by Mr. U. A. Menon.
Manufacture of water pigment finishes for leather.	Read by Mr. M. A. Ghani.
Resin emulsions—finishing auxiliaries	Read by Mr. J. Budaga Rao, C.L.R.I.
Leather finishes—alkyd resins	Read by Mr. T. K. Parthasarathy, C.L.R.I.
Some important binders—Natural and synthetic.	Read by Mr. G. S. N. Murthy.
A pre-requisite for increase in the Indian tanning and leather industry.	Read by Mr. M. A. Ghani, C.L.R.I.

PIGMENT FINISHES FOR LEATHER

BY

E. S. SUBRAMANIAN
(*Handymen Industries Private Ltd., Madras*)

ABSTRACT

Pigment finishes occupy an important position amongst the various finishes at the disposal of the leather finisher. The different materials that go to constitute these finishes are considered.

Pigment finishing of leather appears to have been introduced during the first World War to overcome the shortage of aniline dyestuffs. Although this was adopted as an emergency measure, soon it became a regular feature on account of certain obvious advantages. Leathers with defective grain could be covered up with pigment finishes which gave a more even colouration than the dyes. The use of pigment finishes was later extended even to leathers with good grain surfaces, as it was possible to give an excellent finish due to improvements in the manufacture of the finish. The transformation from dye staining to pigment finishing of leather has been continuous and almost complete as it stands to-day because very rarely we come across leathers finished with aniline dyes.

The modern leather finisher has now at his disposal a range of finishes to choose from—Water pigment finishes, pigment pastes, powder finishes, resin or plastic finishes, cellulose finishes, etc. The very first step in making a leather finish is probably grinding some dry colours in a solution of casein. It is interesting to note that, with all these developments in finish manufacture, the main principle underlying the manufacture of water pigment finish which again is the most widely used type, has remained the same, although a variety of materials go into the composition of the binder. It will not be out of place if we go through the outlines of leather pigment finish manufacture, particularly the aqueous type.

Pigment finishes essentially consist of dry pigment, binding materials such as casein, waxes and plasticisers, and preservatives. The choice of the raw materials plays an important part in the manufacture. Strict control of quality is essential to ensure uniform standards in the final product. Formulations are always done with the primary object that the finish should have good adhesion and should enhance the appearance of the leather and to maintain the finished look even after flexing and folding to which the leathers are normally subjected when manufactured into articles.

A wide variety of pigments can be used from natural earth colours to synthetic organic colours. Earth colours were originally used but after the advent of synthetic precipitated colours like the iron oxides they have fallen into disuse. The main drawback with the natural colours is their dull shade and lower tinting strength as compared to their synthetic counterparts. Iron oxides are invariably used for most browns ; yellow oxides for buff and lighter shades of brown; Chromes for yellow and orange ; synthetic organic colours (sometimes in admixture with inorganic colours) for red, blue and greens ; carbon black for black. The choice of the pigment for each colour should be done with care. If the pigment is neutral, has no reactive group and is inert in character, it would be ideal. Pigments which react in alkaline media should be particularly avoided. Light fastness and dispersability, fineness etc., are other factors to be considered. Instead of starting with dry colours, and then wetting and dispersing them by grinding, it will be easier wherever it is possible, to get precipitated pastes in the form of pulps of various pigments and then compound them with binders etc.

Binder, as the term is generally used, includes all that goes into the formulation of a leather finish except pigments. Of course there are different types of binders suitable for different purposes. Proteinous materials like casein, gelatine or glue form the starting point of most binders. Other important materials are shellac, albumen of blood and egg, synthetic resin emulsions, water soluble resins, bodying agents like gum tragacanth, alginates etc. Casein, as the main constituent of a leather finish, has stood the test of time. The ability to lend itself to glazing with slight adjustments, its availability in fairly uniform quality, its colloidal nature and cost are some of the factors which are responsible for the pre-eminent position of casein in leather finishes in spite of rapid inroads of synthetic materials.

It may not be irrelevant to consider the position of casein with regard to the indigenous leather and leather finishes industries. For a long time this item was under O.G.L. and supplies of good casein were available freely in the market. Recently this item was removed from the O.G.L. because of foreign exchange difficulties. The existence of a few Indian factories who manufacture casein, obviously was a contributory factor for the Government taking this decision. The policy of giving encouragement to indigenous industries by curtailing or banning import of foreign products is no doubt a laudable one. As a matter of fact, the leather finishes industry itself is a beneficiary in this respect for the Government of India rightly felt that the quality of indigenous finishes was equal to the imported products and therefore totally banned the imports of such finishes. The position regarding casein is slightly different. This is an item which is used not only in the leather industry but also in other industries like plywood where it is used to make adhesives. The quantum of demand is probably more in the latter. It has to be unfortunately pointed out that the quality of Indian casein is not upto the standard of the imported varieties like Argentine casein. The standard of casein required for the leather and leather finishes industries is definitely high since the finishes made out of casein have to be stored for considerably long periods of time without deterioration. Several factors have to be taken into account in finding out the suitability of casein to the leather finish industry such as fineness, colour, odour, easy solubility with the minimum amount of alkali and temperature, ability to keep sweet on storage, maintaining original viscosity on storage etc. Considering all these factors, it will be found that the indigenous varieties of casein fall short of the requirements of this industry as compared to the best imported varieties which are eminently suitable. Possibly, the indigenous varieties are suitable for the adhesive industries. Since the quality of indigenous leather finishes has to be kept up to serve the leather industry well, it is imperative that proper type of raw materials like good quality casein is made available to the manufacturers, even if it has to be imported. The total tonnage of casein required for the leather and its auxiliary industries will be too small to make any impression on the foreign exchange position. Under the circumstance, it will not be out of place if a request is made on behalf of the industry to the Government of India, through the Central Leather Research Institute, to grant licences for casein to actual users, to enable the industry to be placed on a firm footing.

Gelatine also can be incorporated in binder although it cannot substitute casein. It possesses very good adhesive power but not the same glazing properties as casein. Advances have been made in Western countries recently acids have also been used to impart varying degrees of flexibility to the resins. These resins already find extensive use in nitrocellulose lacquer formulations. Owing to the inherent toughness and flexibility of these resins, a high ratio of resin to nitrocellulose can be used without affecting the flexibility of the lacquer film and the increased resin content helps film building and gloss. Water dispersed emulsions of these resins are also already in use in paint manufacture because of their ability to seal porous surfaces. As leather finishing is essentially application of extensible films on porous surfaces, these resin emulsions, if suitably modified, may be useful for leather finishing.

3. *Vinyl Resins :* Among the important members of the family are Vinyl Acetate, Polyvinylchloride, Vinylchloride-Vinylacetate copolymer etc. Polyvinylchloride, when unplasticized, is a hard tough resin whilst polyvinyl acetate is softer. When the monomers of these two are mixed and copolymerised the resulting copolymer vinyl resin is tough, chemically inert and insoluble in water and alcohol, but soluble in certain organic solvents. Emulsions of lacquer-in-water type can be made from these solutions and the emulsions thus formed have very good stability.

However, in conclusion, it should be pointed out that development of synthetic resins for leather industry can only be profitable when the monomers required for the manufacture of polymer emulsions are available in our country. At present, this is not the case, and we in the leather industry being but consumers of comparatively small quantities of these resins, will have to await developments in this direction by the paint and plastics industries. Nevertheless a thorough investigation of these resins is worthwhile especially with regard to their compatibility with certain natural resins like shellac which are available in plenty in our country.

NITROCELLULOSE SOLVENTS AND DILUENTS—TYPES AND USES

BY

U. A. MENON

Gordon Woodroffe Leather Manufacturing Co., Madras

ABSTRACT

The different types of solvents used in the preparation of nitrocellulose lacquers are dealt with, with reference to viscosity of resulting solutions, evaporation rate and solvent power.

In the Leather Trade there is always a certain demand for Nitrocellulose Lacquers for production of Upholstery and other types of leathers. These lacquers are required for obtaining a Fast Finish and organic solvents and diluents play a very important part in producing a smooth, flexible waterproof film. The solvents known in the trade can be classified in various ways depending upon their source, solvent power, rate of evaporation etc., but accepting the trade practice they are classed under the following categories :—

A — Active Solvents.
B — Latent Solvents.

Active Solvents : Active or true solvents dissolve nitrocellulose at all conditions and the viscosity increases logarithmically with increasing solid content.

The active solvents are the usual type of esters, ketones and ethers available in wide ranges of molecular weight, boiling range, flash point etc. There is of course in the final analysis no best choice of solvents for lacquer types. The several solvents and diluents have their own merits and the choice will have to depend on the inevitable compromise between cost and performance and the personal preference of the particular formulator.

The Latent types do not, however,, dissolve the nitrocellulose directly but only boost the activity of the true or active solvents. Alcohols are frequently referred to as Latent solvents because part replacement of true solvents raises the amount of diluent, the solvent blend will tolerate, before nitrocellulose is precipitated. If alcohol is used to replace true solvent at a fixed content of nitrocellulose the viscosity of the solution generally falls to a minimum as the proportion of alcohol is increased, after which the viscosity starts to rise, with the result, eventually at higher proportion of alcohol the mixture is no longer a solvent and nitrocellulose is precipitated out.

The effect of increasing the proportion of alcohol to true solvent in a nitrocellulose solution on viscosity is shown below.

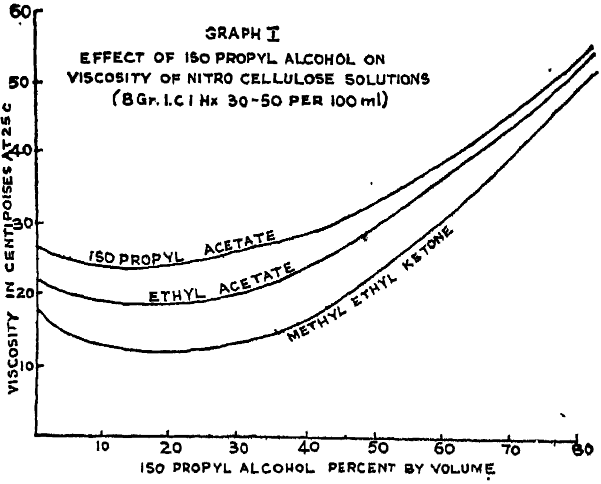

Fig. 1

Diluents do not dissolve nitrocellulose. Solutions of nitrocellulose in mixtures of true solvents and diluents have higher viscosities than equivalent solutions in true solvents alone. This is in contrast to the behaviour which has been described above. Progressive replacement of true solvent by diluent in a nitrocellulose solution leads to gradual increase in viscosity and at a certain point the viscosity starts to increase very rapidly and soon after nitrocellulose is precipitated out.

The Effect of Diluents on Viscosity : The effect of increasing the proportion of diluent to true solvent in a solution of nitrocellulose on viscosity is shown below graphically, for a fixed nitrocellulose content.

The amazing growth of solvent industry can be fairly comprehended when we realise that starting from a few solvents, *viz.*, aliphatic and aromatic hydrocarbons, methyl and ethyl alcohol, acetone, glycerine and turpentine, a giant industry has now grown producing over five hundred different solvents. These are derived from a variety of raw materials and include about half a dozen principal types. One of the fastest growing segments of the solvent industry is the aliphatic chemical or the petro chemical range of solvents.

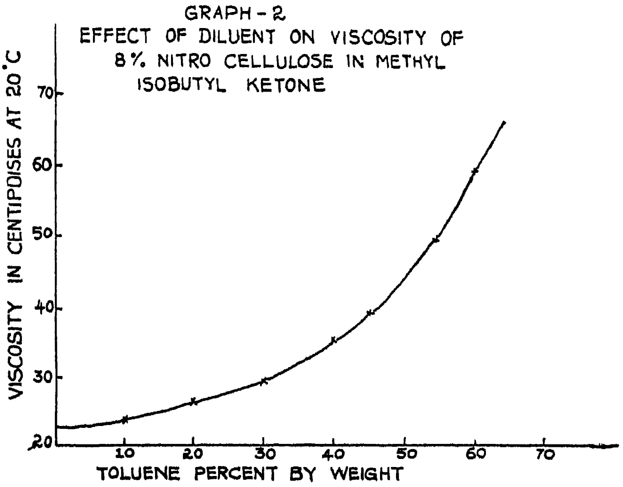

Fig. 2

Solvent acts as a vehicle in a nitrocellulose lacquer and makes it a workable liquid so that it can be applied or spread over a surface. The method of application as well as solid ingredients govern the selection of solvents. A lacquer made for a dip application requires a different solvent from that intended for brush application. Also if we consider spraying lacquers alone some are required to dry slowly and others rapidly. Each of these types is therefore to be formulated with different solvents to fit specific production schedules.

The most important properties of any solvent are :—

(1) Evaporation Rate.

(2) Solvent Power.

Evaporation Rate : The evaporation behaviour is of particular importance in many performance characteristics of nitrocellulose lacquers since they dry simply by evaporation of solvents and undergo no chemical change during film formation. It is indeed because of this requirement that choice of solvents can be made to introduce any desired condition, as for example dry rapidly and this property can be determined without making a fully formulated lacquer. Various methods are used to determine the factor. One of the methods developed by Shell Laboratories in the U.K. designed to estimate as closely as possible the evaporation of solvent is very much made use of in the solvent industry. The method consists in measuring the rate of loss of solvent from a solution of a plasticiser under carefully controlled conditions. A plasticiser solution is chosen instead of a fully formulated lacquer because it is not possible to find a fully formulated lacquer, which would have a resin/nitrocellulose combination soluble in all solvents and non-solvents. Tests with active solvents on nitrocellulose have shown that the use of a plasticiser mixture has very little effect on the results obtained. This is calculated as percentage against time ; when calculating, however, the rates relative to normal butyl acetate is taken as the standard.

Solvent Power : In order to be useful, a solvent must have the power to dissolve a desired material. It is important that a solvent used for nitrocellulose must dissolve nitrocellulose. It is expected that a reduction in viscosity is associated with the power of solvency. Thus a solvent used as a carrier for nitrocellulose permits uniform disrtibution as a thin film over a large area. There is however no one solvent, which possesses all the requirements necessary to make a satisfactory lacquer. A blend of several solvents is therefore necessary to produce a satisfactory lacquer. For securing a homogeneous film and to minimise tendency towards " blushing," particularly in the faster drying lacquers, the solvents should be preferably non-hygroscopic and not miscible with water. The presence of higher boiling solvents, however, will counteract the effect of such fast evaporating solvents which are necessary in such formulations.

The odour of solvents and diluents is of importance as also the toxicity, for most of the lacquers are sprayed indoors where the usual method of spray application may throw a large amount of vapour into the atmosphere in a short time. Exhaust fans may help, but selection of solvents with least objectionable odours and minimum toxicity is desirable.

Until very recent years coal-tar derivatives were the main sources of raw materials for the solvent industry but today petroleum industry is playing a very important role and is the source for most aliphatic solvents and also the source for the largest percentage of aromatic solvents used in the surface coating industry. The introduction of petroleum solvents in the aromatic industry is an outgrowth of the Second World War with the result that we are no longer able to describe the hydrocarbon solvents in reference to their sources of production.

A PRE-REQUISITE FOR INCREASE IN THE INDIAN TANNING AND LEATHER WORKING INDUSTRY

BY

BATLIBOI & Co., MADRAS

ABSTRACT

An appeal is made for liberalising and facilitating import of machinery and equipment needed for tanning and leather working operations.

This symposium has been laying stress on the various aspects of " Leather Auxiliaries " vis-a-vis Indian Tanning Industry. The interesting and exceedingly informative proceedings of this symposium certainly have the effect of getting the attention of the Government focussed upon the need of encouragement to this industry. Such an increased awareness on the part of the Government of India will be ably utilised by the Industrialists concerned to the best advantage of this industry which is vital in the present context of the Indian foreign exchange economy.

We hope it will not be out of place to make certain observations.

It cannot be denied that the great bulk of the Indian Leather Trade is bound to be only in raw, semi-tanned or fully tanned hides and, therefore, comparatively viewing, the scope of finished leather articles may be negligible not only for the time being but may be so for some time to come. Nevertheless, there should be a legitimate aspiration—especially in the light of the much-sought-after export drive—to step up exports of finished leather articles and leather manufactures of all kinds. We should gratefully acknowledge that the seed for such aspiration-potential has already been sown by the Government of India and by different State Governments—chiefly Madras State Government.

But for the initiative taken by the Government of India (through the medium of their Small Industries Service Institutes and the various State Governments) one can dare say that there would have been little knowledge among the general public about the possibilities of fast-production-methods for leather articles—fast but at the same time falling within the scope of a small scale industry.

Tributes are due to the European Experts who are present in India and doing yeoman service here in popularisation of the mechanised production and the related technical know-how. A number of footwear centres have been established and are being set-up.

At the same time we cannot help remarking that while these footwear centres are creating, and are further likely to promote, interest on the part of investors concerned in that line, there is no incentive in other spheres to give shape to such interestedness of those people into concrete materialisation of such industries.

So also is the case with the more primary tanning industry. While more and more information on modern, scientific and mechanised methods of tanning are being made available to the leading and potential tanners, at the same time it has to be admitted that should those tanners become interested in actual acquisition of such machinery and equipments they would find that this to be fraught with much practical hardships in the form of import restrictions.

No doubt, no responsible person can venture to even remotely criticise the import restrictions exercised by the Government which are entirely consequent on the foreign exchange gap. Nevertheless when preferences and priorities are considered, positive and sympathetic considerations should definitely weigh towards relaxation of control over imports of machinery and equipment connected with tanning and leather working operations. Of course there is no ban as such of these imports, but practically even the actual users—especially the private parties—do not find it easy at all to get a licence for imports of bare minimum of such machinery.

The manifold importance of all branches and aspects of leather industry in India cannot be exaggerated and, therefore, it needs no detailed arguments to support a claim for reasonable relaxation and liberalisation of importing regulations for machinery and equipments allied to this industry.

The short-term effect of such a liberalisation would be mainly promotion of small-scale industries, and the long-range effect too, reflect itself proportionately on the foreign exchange earnings.

It is confidently felt, therefore, that this symposium will be doing a right thing if they decide to suitably bring this position and the remedial need to the notice of the concerned authorities.

Discussion

Mr. Subramaniam : How much of casein is produced in India and how much is used by the leather industry ? In what way is Indian casein inferior to the foreign material ?

Mr. Ramakrishnan (Handymen Industries Ltd., Madras) : Correct statistics are not available. Indian casein cannot be preserved without deterioration for more than 7 or 8 days whereas foreign samples stay for 3 to 4 months. Further Indian casein is not tolerant to formaldehyde.

Dr. Bhaskaran (C.L.R.I.) : In other countries there is excess of milk produced and casein is prepared from the excess milk. In our country there is actually shortage of milk and so the position with regard to casein could improve only with improvement in the position of milk supply.

Dr. Y. Nayudamma : The greater part of Indian leather is made in villages and towns where the tanner has no facility to finish the leather. So if a finished leather could be obtained by vegetable tannage without spraying, plating and so on, but just using a simple finish which could be applied with a cloth or brush, it would be much helpful. I would like to know whether anybody would give the answer.

Mr. Ramakrishnan : The leather finishes supplied by us would be suitable in this regard for they are mixed with water, then applied with the brush and the whole thing is rounded off with glazing.

Dr. Y. Nayudamma : I want leathers to be finished even without glazing. If we could get glazed finish without use of machinery we would be contributing towards national economy.

Mr. Ramakrishnan : Such a finish has been developed. However, I would suggest that the Central Leather Research Institute, itself take up this problem.

Mr. Murthy : I suggest that shellac resins could be applied so as to dry off quickly provided they are compatible with casein.

Mr. S. C. Das, (Indian Leather Technologists' Association, Calcutta) : Water pigments are available in plenty in India and these could be used. For ironing, emulsion could be applied.

Mr. Bhagwat, (Modern Tanneries, Bombay) : In our Bombay Society of Tanners, we have been preparing a finish without using pigments but using shellac. It is fairly water proof and has given good results. It is finished with the help of glass. However, only red leather could be produced

Dr. Y. Nayudamma : I wish to thank the Modern Tannery Representative. I suggest that my colleagues in S.I.S.I. and All India Khadi and Village Industries Commission, get in touch with them and help in showing these processes to the tanners.

Mr. Leitensdorfer (Bata Shoe Co. Ltd.) : Any finish supplied in India lacks technical data. While the commercial secrets could be withheld, some essential details like how much casein is present and how much need be added could be indicated. Such information is given in other countries.

Mr. Sushil Sarkar, (Indian Leather Technologists' Association, Calcutta) : In some brown shoes, black stains are obtained. I would like to know the cause of this. It is said they are due to indigenous pigment finishes.

Dr. Y. Nayudamma : The black stains occur only with yellow pigments, possibly due to impurities present in chromate. I believe this trouble has been now rectified.

It is necessary that we go down to the level of the village tanner and supply him with the ready solution to be applied. Thanks to the efforts of my colleagues Shri Parthasarathy and Shri Ganesan; some amount of success has been achieved in preparing finishes giving gloss without glazing. However, some more work is to be done before quite glossy leathers could be obtained. The economics also have to be worked out.

Mr. A. Ganesan : We have been working on alkyd resin emulsions so as to apply a water based, but water proof glossy finish. Certain unexpected difficulties were encountered in incorporating pigments in these alkyd resins. The degree of absorption of the driers was much more than anticipated. Certain carbon blacks used absorbed plenty of the driers and there was difficulty in drying the finish. Not only the chemical composition of the pigment but also the physical condition of the pigment is important. There is difficulty due to different portions of leather absorbing to different extents. However, it is hoped to be able to produce a satisfactory finish before long.

Mr. G. S. Rama Iyer (C.L.R.I.) : Shortage of carnauba wax is a problem facing not only the leather finishing industry, but also the polishes industries. The National Chemical Laboratory have prepared a modified sugar cane wax which has been tried in this Institute in shoe cream formulations with good results, as a substitute for carnauba wax. Some years ago, the Forest Research Institute published details of preparation of a substitute for carnauba wax. A more or less similar substitute wax has been prepared in this Institute and has been tried in the form of emulsion for finishing sole leather. Good finish has been obtained.

The disadvantage in using natural rubber latex in water pigment finishes is said to be the resulting tackiness. It is suggested that incorporation of large amount of casein in the emulsion would minimise the tackiness.

Mr. M. A. Ghani (C.L.R.I.) : More than 5% latex was always troublesome because the finish cannot be glazed.

Mr. Ramakrishnan : I would like to know whether the modified sugar cane wax was bleached.

Mr. Mhasker, (National Chemical Laboratory, Poona) : We have supplied a sample of the modified wax which is of very pale brown colour.

Mr. M. A. Ghani : As regards the problem of finishing by the village tanner, I would suggest that finishing could be at a centre organised by the handicrafts board where all necessary facilities could be given. The village tanners would then bring their leathers to this centre for finishing.

Mr. S. Nagarajan (S.I.S.I.) : The Small Industries Service Institute is doing extension service work on behalf of the different national laboratories. The tanners are coming to the technical personnel of the Small Industries Service Institute.

Dr. Y. Nayudamma : I am asking you to go to the tanners and not the tanners to come to you.

Mr. Nagarajan : We cannot take the machines to the tanners.

Chairman : Then eliminate machines.

Mr. Das, (Indian Leather Technologists' Association, Calcutta) : Are there data regarding manufacture of water pigments ? Are these pigment finishes tested to be suitable ? Since the Government have banned import of these finishes, the data about the quality and quantity are necessary.

Dr. Y. Nayudamma : I wish I were in a position to answer this question properly. We do test all available Indian manufactured products, be they syntans or anything. However, we do not like the firms to make use of the Central Leather Research Institute name to sell the products. It is our considered opinion that the leather finishes made in India are equal to those imported in several respects except in the case of yellow pigments, and now we are told that the Calcutta and Madras firms are in a position to supply even this yellow pigments in satisfactory quality.

Chairman : The complaint of the tanner has been that the quality of the finishes supplied by Indian manufacturers is not always uniform.

Mr. Ramakrishnan : I can confidently assure you of uniform quality on behalf of the two firms in Calcutta and Madras. Our friends from Bata and Gordon Woodroffe will vouchsafe for this.

Mr. Leitensdorfer : Not quite so.

Mr. G. S. N. Murthy (Gordon Woodroffe Leather Mfg. Co.) : There are minor variations.

Mr. S. C. Das : Myrobalan extract is available in plenty in India. Goran extract could be used in boilers. Central Leather Research Institute must take up this question and see whether myrobalan extract is also suitable. What conclusions could be drawn on the comparative merits and demerits of chrome retanned and chrome leathers ?

Mr. M. A. Ghani : The work regarding extracts is already under investigation. Different extracts have been prepared for testing.

As regards the assessment of the quality of different types of leathers this work is being done in this Institute. However, the processes of all the different types of tannages have to be studied before they are standardised.

Mr. R. Selvarangan : Protein finishes do not fill and flex and do not have scuff and water resistance. So they cannot be used on Indian hides which usually have defective grain. Protein finishes could be suitably used only with glazed kid and fine calf where the natural feel and grain pattern are to be retained. A combination of resin and lacquer finishes would be better. The resin finish covers grain defects considerably and lacquer finish has got good water and scuff resistances. The lacquer emulsion can be padded instead of sprayed. The body giving material would effectively cover up the grain defects and the lacquer will give the necessary resistance properties. Since acrylic resins and lacquer are very costly, we could have gum, shellac, casein, pigments, etc., in the aqueous phase. As for the resins to be used in the solvent phase they should be available cheaply and from indigenous sources.

The following draft resolutions of the Leather Auxiliaries Sub-Committee were then placed before the general body of the Symposium by Dr. S. K. Barat.

(1) That an All India Leather Fair be made an annual feature which should be organised in winter every year and held in important centres of the Leather Industry by rotation.

(2) That information and statistical data regarding the actual and potential availability of some of the promising indigenous tanning materials be made known to the tanning industry.

(3) That a ' Myrobalan Board ' on the lines of the Coffee and Tea Boards, be constituted for the collection, grading and marketing of myrobalan nuts and also encouraging plantations wherever and whenever necessary.

(4) That satisfactory methods for proper extraction, grading and marketing of fish oil of the west coast be standardised and the industry organised on the small scale sector for the benefit of the tanning industry.

(5) That a survey be made of the requirements of leather auxiliaries and the potential capacity of the existing plants assessed so that the manufacture can be conveniently developed as a small scale industry.

The resolutions were accepted and passed unanimously. The session and the Symposium came to a conclusion with a vote of thanks by Dr. Y. Nayudamma.

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